Facile Synthesis of Fluorinated Phosphonates *via* Photochemical and Thermal Reactions

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Received April 28, 1997[⊗]

Abstract: Under UV irradiation (254 nm) at ambient temperature, a degassed mixture of $(EtO)_2POP(OEt)_2$ and R_fI {R_f = CF_3, C_2F_5, C_4F_9, C_6F_{13}, $(CF_3)_2CF$, $CF_2CF{=}CF_2$, $ClCF_2CF_2$, $BrCF_2CF_2$, C_6F_5, $ClCF_2CFClCF_2CF_2$, $I(CF_2)_3$, $I(CF_2)_4$, $FO_2S(CF_2)_4$, $FO_2S(CF_2)_2O(CF_2)_2$} affords the fluorinated phosphonite, $[R_fP(OEt)_2]$. Oxidation of the phosphonites, $[R_fP(OEt)_2]$, with Me_3COOH gave the corresponding fluorinated phosphonates, $(EtO)_2P(O)R_f$ (**1**−**14**), in 35−80% isolated yields. CF_3CCl_2I reacts with $(EtO)_2POP(OEt)_2$ at room tempearture in the absence of UV irradiation to afford $[CF_3CCl_2P(OEt)_2]$ which upon oxidation gave a 52% yield of $CF_3CCl_2P(O)(OEt)_2$ (**15**). The reaction of $(EtO)_2POP(OEt)_2$ and R_fI (R_f = $ClCF_2CF_2$, $BrCF_2CF_2$, C_2F_5) at 125 °C in the presence of $Me_3COOCMe_3$ and subsequent oxidation of the resultant phosphonites afforded phosphonates (**2**, **7**, and **8**) *albeit* in lower yields (49−62%) compared to those of the photochemical reaction (58−80%). $(RO)_2P(O)CF_2CF_2I$ (R = Et, *i*-Pr) (**16** and **17**) was obtained (42−48%) when a degassed mixture of $(RO)_3P$ and $BrCF_2CF_2I$ was subjected to UV irradiation (254 nm) at ambient temperature *via* a unique photochemical transformation.

Introduction

Phosphate esters constitute one of the most significant structural entities in all living organisms, and the preparation of a number of new phosphonates and their biochemical studies have been reported.[1] The first preparation of a fluorinated phosphonate, $(EtO)_2P(O)CF_2H$, was reported by Soborovskii and Baina 37 years ago.[2] Since then, relatively few fluorinated phosphonates have been reported, compared to their nonfluorinated analogues, although it is well documented that incorporation of fluorine into biologically important compounds results in enhanced activity and stability while a steric demand similar to the hydrogen atom is exhibited.[3] This dearth of fluorinated analogues can be attributed to the lack of synthetic procedures, since methods commonly used for the preparation of phosphonates cannot usually be applied to fluorinated analogues.

In recent years, the desirable properties conferred upon fluorine substitution have caused an increased interest in the study of fluorinated phosphonates.[4,5] Blackburn and coworkers[6] suggested that (α,α-difluoroalkyl)phosphonates should mimic phosphate esters better than the corresponding phosphonates. Therefore, fluorinated phosphonates have been investigated as phosphonate analogues,[4−6] enzyme inhibitors,[7] fuel cell electrolytes,[8] and chelating agents.[9] The continued interest in these compounds is manifested by the recent syntheses of a number of novel fluorinated bisphosphonates, bisphosphonic acids,[10−13] and phosphonic acids.[14,15]

Soborovoskii and Baina prepared $(EtO)_2P(O)CF_2H$ *via* reaction of the diethylphosphite anion with chlorodifluoromethane (eq 1).[2] Later, synthesis of dialkyl (bromodifluoromethyl)-

$$(EtO)_2P(O)Na + HCF_2Cl \longrightarrow (EtO)_2\overset{\overset{O}{\|}}{P}CF_2H \quad (1)$$

51%

phosphonate, from a trialkylphosphite and CF_2Br_2, was reported (eq 2).[16] Although, mechanistically, both of these reactions (eqs

[⊗] Abstract published in *Advance ACS Abstracts,* September 1, 1997.

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S0002-7863(97)01345-0 CCC: $14.00

$$(EtO)_3P + CF_2Br_2 \xrightarrow[\text{reflux}]{\text{Ether}} (EtO)_2P(O)CF_2Br \quad (2)$$
95%

1 and 2) appear to be S_N2 type displacements, they actually involve the generation and subsequent capture of difluorocarbene.[17−20] Thus, the above methods are specific for difluoromethyl analogues and cannot be extended to higher homologues. Photochemical preparation of $(EtO)_2P(O)R_f$ {R_f = CF_3, C_6F_5} *via* treatment of a mixture of $(EtO)_3P$ and CF_3I or C_6F_5I has been reported;[21] however, this procedure was not successful for the synthesis of higher homologues.[17] In 1981, Kato and Yamabe reported the synthesis of $(EtO)_2P(O)R_f$ (R_f = C_6F_{13}, C_4F_9, $(CF_3)_2CF$) in 41−71% yield *via* a thermally-induced radical reaction of tetraethylpyrophosphite and the respective *F*-alkyl iodide.[22] Recently, the reaction of $(EtO)_2P(O)Cl$ and *in situ* generated R_fMgX {$R_f = C_6F_{13}$, $Cl(CF_2)_4$, $Cl(CF_2)_6$, $Cl(CF_2)_8$, and $FO_2S(CF_2)_2O(CF_2)_4$} at −50 °C was reported to afford the corresponding *F*-alkylphosphonates.[23] In a recent paper,[24] we reported the preparation of dialkyl (*β*-halotetrafluoroethyl)phosphonates *via* thermally- and photochemically-induced radical reactions.

As part of our program, we investigated the synthesis of fluorinated phosphonates by various approaches. In this paper, we describe the facile synthesis of a number of novel as well as previously reported dialkyl fluorinated phosphonates from readily available substrates, in good yields, *via* photochemically- and thermally-induced radical reactions.

Results and Discussion

Kato and Yamabe prepared $R_fP(O)(OEt)_2$ {$R_f = C_6F_{13}$, C_4F_9, and $(CF_3)_2CF$} in 41−71% yield *via* thermally-induced radical reaction by heating a mixture of $(EtO)_2POP(OEt)_2$ and the appropriate R_fI in the presence of di-*tert*-butyl peroxide in an autoclave.[22] However, the preparation of a functionalized phosphonate, for example, a dialkyl (*β*-halo or *ω*-halofluoroalkyl)phosphonate, has not been demonstrated by this procedure. We sought a milder procedure which avoids heating the reaction mixture with a peroxide at high temperature and which could be utilized for the synthesis of *F*-alkyl as well as functionalized *F*-alkyl phosphonates. We report a convenient photochemical method that meets both criteria, as discussed below.

Scheme 1

$$(EtO)_2P\text{-}O\text{-}P(OEt)_2 + R_fI \xrightarrow[\text{amb. temp}]{h\upsilon} [(EtO)_2PR_f]$$
$$[(EtO)_2PR_f] \xrightarrow[\text{MeOH}]{-20^\circ C,\ Me_3COOH} (EtO)_2P(O)R_f \quad 35\text{-}80\%$$

[R_f = CF_3, C_2F_5, C_4F_9, C_6F_{13}, $(CF_3)_2CF$, CF_2-CF=CF_2, $ClCF_2CF_2$, $BrCF_2CF_2$, C_6F_5, $ClCF_2CFClCF_2CF_2$, $I(CF_2)_3$, $I(CF_2)_4$, $FO_2S(CF_2)_4$, and $FO_2S(CF_2)_2O(CF_2)_2$]

Table 1. Preparation of Fluorinated Phosphonates

no.	method	product	isolated yield (%)[b]
1	A	$(EtO)_2P(O)CF_3$	63
2	A, B	$(EtO)_2P(O)C_2F_5$	58, 49
3	A	$(EtO)_2P(O)CF(CF_3)_2$	63
4	A	$(EtO)_2P(O)C_4F_9$	69
5	A	$(EtO)_2P(O)C_6F_{13}$	79
6	A	$(EtO)_2P(O)CF_2CF{=}CF_2$	59
7	A, B	$(EtO)_2P(O)CF_2CF_2Br$	80, 62
8	A, B	$(EtO)_2P(O)CF_2CF_2Cl$	75, 53
9	A	$(EtO)_2P(O)(CF_2)_3I$	37
10	A	$(EtO)_2P(O)(CF_2)_4I$	35
11	A	$(EtO)_2P(O)C_6F_5$	35
12	A	$(EtO)_2P(O)CF_2CF_2CFClCF_2Cl$	72
13	A	$(EtO)_2P(O)CF_2CF_2OCF_2CF_2SO_2F$	57
14	A	$(EtO)_2P(O)(CF_2)_4SO_2F$	64
15	C	$(EtO)_2P(O)CCl_2CF_3$	52
16	D	$(EtO)_2P(O)CF_2CF_2I$	42
17	D	$(i\text{-}PrO)_2P(O)CF_2CF_2I$	48

[a] Method A $(EtO)_2POP(OEt)_2 + R_fI$, under UV irradiation (254 nm); method B $(EtO)_2POP(OEt)_2 + R_fI + Me_3COOCMe_3$, at 125−130 °C; method C $(EtO)_2POP(OEt)_2 + R_fI$, at room temperature in the absence of UV irradiation (254 nm); method D $(RO)_3P + R_fI$ (R = Et or *i*-Pr), under UV irradiation (254 nm). [b] All yields are based on the respective fluorinated iodide.

Under UV irradiation (254 nm) at ambient temperature, a degassed mixture of $(EtO)_2POP(OEt)_2$ and a fluorinated iodide afforded the corresponding phosphonite, $[(EtO)_2PR_f]$. A number of fluorinated iodides, primary, secondary, aromatic, allyl, *β*-halo, *ω*-halo, α,*ω*-dihalo, and substituted *F*-alkyl, could be employed (Scheme 1). Although the phosphonites were not isolated, they could be characterized by $^{31}P\{^1H\}$ NMR analysis, since the difference in chemical shifts between the phosphonite and phosphonate is typically more than 130 ppm.[24,25] Oxidation of the *in situ* generated phosphonites with Me_3COOH in methanol at −20 °C afforded the corresponding phosphonates (Scheme 1). By this method, the new phosphonates (**2**, **7**−**10** and **12**−**14**), as well as previously reported phosphonates, (**1**, **3**−**6**, and **11**), were obtained in 35−80% yields (Table 1). Purification of the phosphonates was best accomplished by frac-

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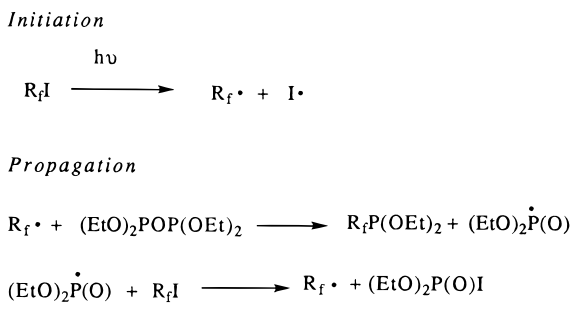
(25) For example, the proton-decoupled ^{31}P NMR δ values for $[(EtO)_2PCF_2CF_2Cl]$ and $(EtO)_2P(O)CF_2CF_2Cl$ are 144.8 (tt) and 0.23 (tt) ppm, respectively; similarly, $^{31}P\{^1H\}$ NMR δ values for $[(EtO)_2PC_6F_{13}]$ and $(EtO)_2P(O)C_6F_{13}$ are 144.5 and 0.81 ppm, respectively.

Scheme 2



tional distillation or column chromatography; the latter always gave better yields, since some decomposition occurs in the former case. This interesting photochemical conversion can be conveniently carried out in a quartz vessel at 254 nm; at 300 nm a slight decrease (~5%) in the yields of the phosphonates was observed.

When a degassed mixture of $(EtO)_2POP(OEt)_2$, $C_6F_{13}I$, and 1-heptene (1.2:1:1) was irradiated (254 nm), ^{19}F and $^{31}P\{^1H\}$ NMR analyses of the reaction mixture revealed the formation of the adduct, $CH_3(CH_2)_4CHICH_2C_6F_{13}$; no $[(EtO)_2PC_6F_{13}]$ was detected. On the other hand, heating a degassed mixture of $(EtO)_2POP(OEt)_2$ and $C_6F_{13}I$ (1.2:1) to 100−110 °C for 9 h did not afford any detectable amount of $[(EtO)_2PC_6F_{13}]$. A possible mechanism for the photochemical transformation is illustrated in Scheme 2. The photolytic cleavage of R_fI affords $R_f^{\bullet}$ and $I^{\bullet}$, in the initiation step. Subsequent reaction of $R_f^{\bullet}$ and $(EtO)_2POP(OEt)_2$ results in $(EtO)_2PR_f$ and $(EtO)_2P(O)^{\bullet}$; $(EtO)_2P(O)^{\bullet}$ abstracts an iodine atom from the perfluoroalkyl iodide generating $R_f^{\bullet}$ which continues the chain process.

The photochemically-induced radical reaction can also be extended to the preparation of *ω*-iodo-*F*-alkylphosphonates, $(EtO)_2P(O)(CF_2)_3I$ and $(EtO)_2P(O)(CF_2)_4I$, by irradiation (4 h) of a mixture of the diiodide, $I(CF_2)_nI$ (n = 3, 4), and tetraethylpyrophosphite in a 1 to 1.2 ratio, followed by oxidation. Requisite 1,3-diiodoperfluoropropane was prepared, in 68% yield, from perfluoroglutaryl chloride *via* a reported procedure.[26] The yields of the *ω*-iodophosphonates were generally low since the product iodophosphonites react further to form the bisphosphonites;[12] the best isolated yields of **9** and **10** were 37 and 35%, respectively. In addition, small amounts (5−10%) of $(EtO)_2P(O)(CF_2)_nH$ were also observed. If excess tetraethylpyrophosphite is employed, the exclusive formation of bisphosphonites could be effected in good yield.[12]

Reaction of a degassed mixture of ICF_2CF_2I and tetraethylpyrophosphite under photochemical conditions afforded only $F_2C{=}CF_2$; formation of $[(EtO)_2PCF_2CF_2I]$ was not observed by ^{31}P and ^{19}F NMR analyses. However, UV irradiation of a mixture of XCF_2CF_2I (X = Cl, Br) and $(EtO)_2POP(OEt)_2$ and subsequent oxidation of the resultant phosphonite with Me_3COOH furnished $(EtO)_2P(O)CF_2CF_2Cl$ (**8**) and $(EtO)_2P(O)CF_2CF_2Br$ (**7**) in 75 and 80%, respectively.[24] When a degassed mixture of $F_2C{=}CFI$ and $(EtO)_2POP(OEt)_2$ was subjected to UV irradiation, no vinylphosphonite was detected by ^{19}F NMR analysis. However, reaction of $F_2C{=}CFCF_2I$ and tetraethylpyrophosphite under UV irradiation resulted in F-allylphosphonite, which upon subsequent oxidation afforded the corresponding phosphonate (**6**) in 59% yield. Similarly, substituted *F*-alkyl iodides $ClCF_2CFClCF_2CF_2I$, $ICF_2CF_2OCF_2CF_2SO_2F$, and $I(CF_2)_4SO_2F$ reacted readily with $(EtO)_2POP(OEt)_2$ to afford the respective phosphonites. After oxidation with Me_3COOH, the phosphonates **12**−**14** were obtained in 57−72% yield. CF_3CCl_2I was so reactive that it reacted even at room temperature without UV irradiation.

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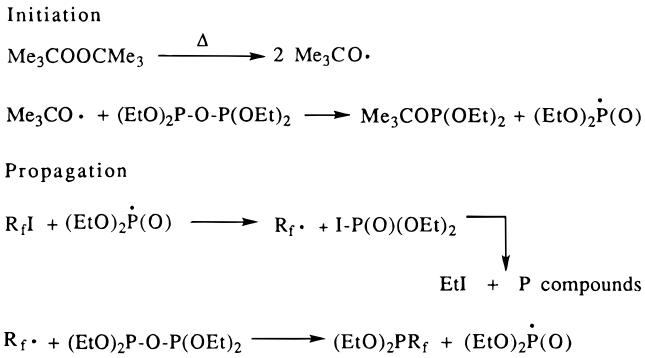
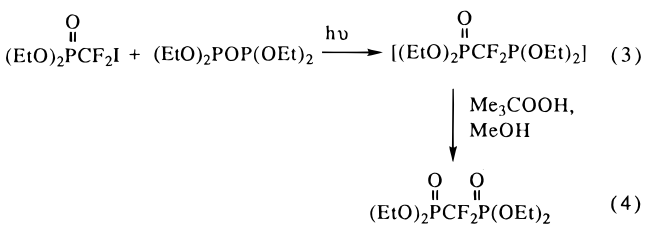
Scheme 3



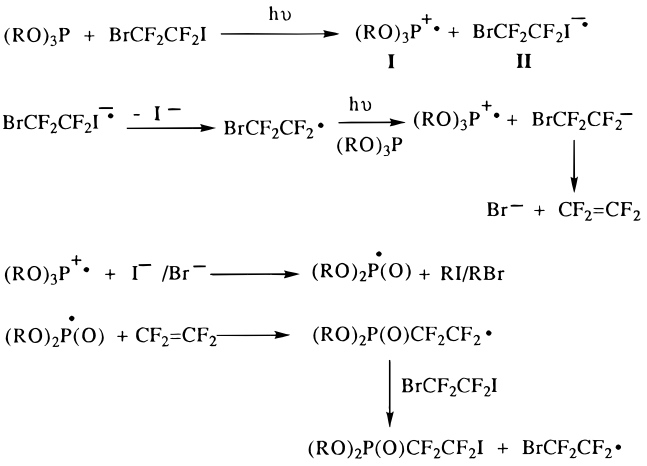
The photochemical procedure can also be extended to the preparation of bisphosphonates.[24] For example, the reaction of $(EtO)_2P(O)CF_2I$ and $(EtO)_2POP(OEt)_2$ under UV resulted in the corresponding mixed P^{III} and P^V intermediate $[(EtO)_2P(O)CF_2P(OEt)_2]$, which affords the bisphosphonate, $(EtO)_2P(O)CF_2P(O)(OEt)_2$ upon oxidation (eqs 3 and 4). The P^{III}-P^V intermediate can easily be identified in the ^{31}P NMR spectrum, since the chemical shifts of the two P atoms differ by more than 130 ppm. Similarly, the irradiation of $I(CF_2)_nI$ (n = 3, 4, 6) and $(EtO)_2POP(OEt)_2$ resulted in the corresponding bisphosphonites, $[(EtO)_2P(CF_2)_nP(OEt)_2]$, which on oxidation afforded the respective bisphosphonates, $(EtO)_2P(O)(CF_2)_nP(O)(OEt)_2$.[24] Thus, the photochemical reaction is a general and versatile procedure that can be employed for the preparation of a variety of fluorinated phosphonates and bisphosphonates.



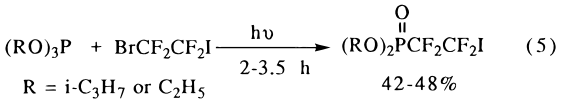
We were interested in extending the Kato−Yamabe reaction[22] for the preparation of *β*- and *ω*-halo-*F*-alkylphosphonates. Thus, when a degassed mixture of ICF_2CF_2I and $(EtO)_2POP(OEt)_2$ was heated at 125 °C in the presence of $Me_3COOCMe_3$, only the formation of $CF_2{=}CF_2$ was observed by ^{19}F NMR analysis of the reaction mixture. On the other hand, $BrCF_2CF_2Br$ was found to be unreactive under the same conditions. In contrast, when ICF_2CF_2X (X = Br or Cl) was employed, $(EtO)_2P(O)CF_2CF_2Br$ (**7**) or $(EtO)_2P(O)CF_2CF_2Cl$ (**8**) could be obtained in 62 and 53% yields, respectively.[24] Similarly, $(EtO)_2P(O)CF_2CF_3$ (**2**) could also be prepared (49%) from CF_3CF_2I and $(EtO)_2POP(OEt)_2$. As noted in Table 1, the photochemical procedure afforded **7**, **8**, and **2** in higher yields (80, 75, and 58%, respectively) compared to the thermally-induced reaction. For ICF_2CF_2I, loss of iodine radical from $ICF_2CF_2^{\bullet}$ to afford $F_2C{=}CF_2$ is faster than the capture of this radical by pyrophosphite. A possible mechanism is outlined in Scheme 3.[22] The reaction proceeds *via* thermally-generated *t*-$BuO^{\bullet}$, which in turn furnishes $R_f^{\bullet}$. Subsequent reaction of $R_f^{\bullet}$ with tetraethylpyrophosphite affords the corresponding phosphonite and phosphoryl radical, as depicted in Scheme 3.

Since, diethyl (2-iodotetrafluoroethyl)phosphonate, $(EtO)_2P(O)CF_2CF_2I$, could not be obtained either by thermal or photochemical reaction of $(EtO)_2POP(OEt)_2$ and ICF_2CF_2I, we

Scheme 4



investigated an alternative approach for its preparation.[27] Thus, when a degassed mixture of $(RO)_3P$ and ICF_2CF_2I was irradiated (254 nm) at ambient temperature, only the formation of $F_2C{=}CF_2$ was observed; the outcome was the same when the reaction mixture was heated to 100 °C. The reaction of $(EtO)_2PONa$ with XCF_2CF_2I (X = Cl, Br) also resulted in $F_2C{=}CF_2$ formation. However, when $BrCF_2CF_2I$ was employed instead of ICF_2CF_2I, $(RO)_2P(O)CF_2CF_2I$ [R = Et or *i*-Pr] was obtained in 42−48% yields (eq 5) with no detectable amount of bromo derivative![24] The yield was optimum when the ratio of $(RO)_3P$ to $BrCF_2CF_2I$ was 2 to 1.



Our proposed mechanism[24] for this remarkable transformation is illustrated in Scheme 4. Photoinduced electron transfer between the phosphite and 1-bromo-2-iodotetrafluoroethane produces the radical cation, **I**,[28−30] and radical anion, **II**, respectively. A second electron transfer to **II** affords the unstable $BrCF_2CF_2^-$, which eliminates Br^- to generate $F_2C{=}CF_2$. Phosphoryl radical results on dealkylation of **I** by either I^- or Br^-. Subsequent addition of phosphoryl radical to the tetrafluoroethylene[31] results in the formation of $(RO)_2P(O)CF_2CF_2^{\bullet}$, which, in the last step, abstracts an iodine atom from the starting ethane to afford $(RO)_2P(O)CF_2CF_2I$ and $BrCF_2CF_2^{\bullet}$; the latter continues the chain process.

One might ask why ICF_2CF_2I does not react with $(EtO)_3P$ to give $(EtO)_2P(O)CF_2CF_2I$? Since the rates of different steps in the proposed mechnism (Scheme 4) are not known at present, one cannot answer the above question with certainty. However, it is possible that for ICF_2CF_2I, the dissociation of $ICF_2CF_2^{\bullet}$ or $ICF_2CF_2^-$ (to $F_2C{=}CF_2$ and $I^{\bullet}$ or I^-, respectively) is faster than the dissociation of $BrCF_2CF_2^{\bullet}$ or $BrCF_2CF_2^-$. One would expect the cleavage of the weaker C−I bond, compared to that of the stronger C−Br bond, energetically to be more favorable, whether induced photochemically or thermally. For example, when a mixture of $(EtO)_2POP(OEt)_2$ and ICF_2CF_2I was heated under degassed conditions, quantitative formation of $F_2C{=}CF_2$ was observed. For $BrCF_2CF_2I$, generation of $F_2C{=}CF_2$ appears to be slow compared to that of ICF_2CF_2I, since we could detect small amounts (2−5%) $BrCF_2CF_2I$ still left in the reaction mixture after irradiation for 3.5 h.[24] Thus, the loss of $I^{\bullet}$ from $ICF_2CF_2^{\bullet}$ is faster than the capture of this radical by pyrophosphite. Also, treatment of ICF_2CF_2I with either $(EtO)_2POP(OEt)_2$ or $(RO)_3P$, under photochemical or thermal (100 °C) conditions, resulted in $F_2C{=}CF_2$ only. In any case, the $ICF_2CF_2^{\bullet}$ generated, under thermal or photochemical conditions, has "limited" stability. Thus, for the last step in Scheme 4, no ICF_2CF_2I is left for the abstraction of the $I^{\bullet}$ atom by $(EtO)_2P(O)CF_2CF_2^{\bullet}$ if it is formed at all. Alternatively, $(RO)_2P(O)^{\bullet}$, in principle, can add to $F_2C{=}CF_2$ to give $(RO)_2P(O)CF_2CF_2^{\bullet}$ (Scheme 4) which in turn can add to more $F_2C{=}CF_2$ in a chain reaction (to give a polymer) or can dimerize to $(RO)_2P(O)(CF_2CF_2)_2(O)P(OR)_2$. However, we were unable to detect the formation of these species by ^{19}F and ^{31}P NMR spectral analyses of the reaction mixture.

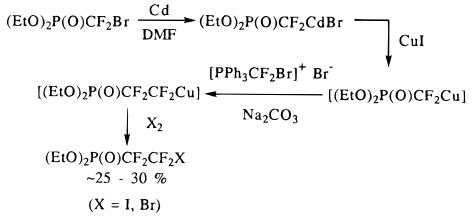
The $^{13}C\{^1H\}$ NMR spectrum of $(RO)_2P(O)CF_2CF_2X$ (R = Et, *i*-Pr; X = Cl, Br, I) for $-CF_2CF_2X$ region for compounds **7**, **8**, **16**, and **17** exhibited a triplet of doublets of triplets (tdt) for the α-C atom attached to the phosphorus and a triplet of triplets of doublets (ttd) for the *β*-C atom. For example, $^{13}C\{^1H\}$ NMR spectrum of compound **16** exhibited a tdt at δ 111.3 ppm ($^1J_{C,F}$ = 273 Hz, $^1J_{P,C}$ = 201 Hz, $^2J_{C,F}$ = 37 Hz) and a ttd at δ 97.3 ppm ($^1J_{C,F}$ = 317 Hz, $^2J_{C,F}$ = 37 Hz, $^2J_{P,C}$ = 14 Hz), for α- and *β*-carbon atoms attached to the P atom, respectively. The experimental and simulated[32] $^{13}C\{^1H\}$ NMR spectra for the $>P(O)CF_2CF_2I$ region for **16** are illustrated in Figure 1.

In summary, photochemical reaction of tetraethylpyrophosphite and fluorinated iodides followed by oxidation affords the corresponding phosphonates, in good yields. A variety of fluorinated iodides, *F*-alkyl, substituted *F*-alkyl, *F*-aryl, *F*-allyl, *β*-halo-*F*-alkyl, *ω*-halo-*F*-alkyl, *ω*-fluorosulfonyl-*F*-alkyl, and substituted *F*-alkyl, can be employed. Dialkyl (*β*-iodotetrafluoroethyl)phosphonates were obtained in moderate yields by the reaction of trialkylphosphite and $BrCF_2CF_2I$ under photochemical conditions. The procedures described in this paper represent convenient and simple routes to some of the previously reported as well as new fluorinated phosphonates. We anticipate that these interesting phosphonates will serve as precursors for the development of biologically important phosphonate-derived compounds and fuel cell electrolytes.

Experimental Section

General. All boiling points are uncorrected. ^{19}F, ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectra were recorded on a JEOL FX90Q or Bruker AC-300 spectrometer. All chemical shifts are reported in parts per million (ppm) downfield (positive) of the standard. ^{19}F NMR spectra

(27) Our first approach to the synthesis of dialkyl (*β*-halotetrafluoroethyl) phosphonates utilized the organometallic reagent derived from $(EtO)_2P(O)CF_2Br$, as shown below. Although the target phosphonates could be obtained, the yields were consistently low and multiple carbene insertions to the Cu−C bond in the $(EtO)_2P(O)CF_2Cu$ could not be avoided.



(28) Bakkas, S.; Julliard, M.; Chanon, M. *Tetrahedron* **1987**, *43*, 501.

(29) ESR studies on radical cations, $(MeO)_3P^{\bullet+}$ and $(MeO)_2HP^{\bullet+}$, have been reported: (a) Hasegawa, A.; McConnachie, G. D. G.; Symons, M. C. R. *J. Chem. Soc., Faraday Trans. 1* **1984**, *80*, 1005. (b) Janes, R.; Symons, C. R. *J. Chem. Soc., Faraday Trans. 1* **1990**, *86*, 2173. Recently, the formation of triethylphosphite radical cation under photochemical conditions has been reported.[30]

(30) Yasuda, M.; Yamashita, T.; Shima, K. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 938.

(31) Addition of radicals to $F_2C{=}CF_2$ is well-known: Haszeldine, R. N. *J. Chem. Soc.* **1953**, 3761.

(32) Spectral simulation programs were designed and written by Dr. W. E. Bennett, University of Iowa.

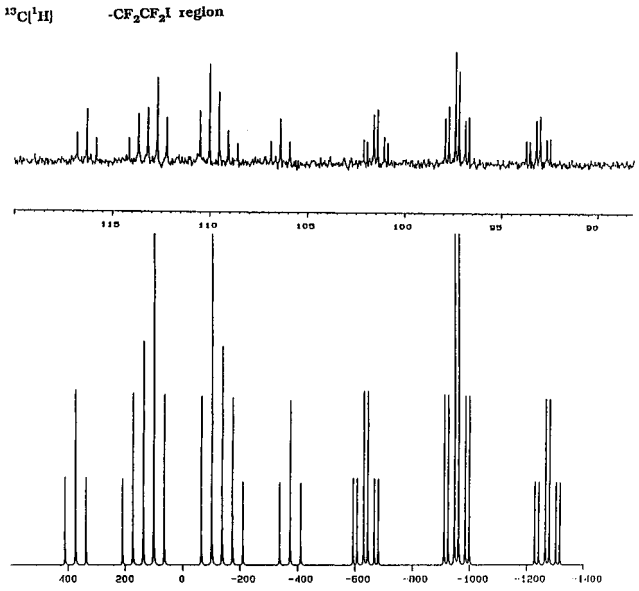


Figure 1. Part of the $^{13}C\{^1H\}$ NMR spectrum of $(EtO)_2P(O)CF_2CF_2I$; simulated (lower trace) and experimental (upper trace).

are referenced against internal $CFCl_3$, ^1H and $^{13}C\{^1H\}$ NMR spectra against internal tetramethylsialne, and $^{31}P\{^1H\}$ NMR against external H_3PO_4. FT-IR spectra were recorded as CCl_4 solutions. Mass spectra were acquired from a VG ZAB mass spectrometer operating at 70 eV in the electron impact (EI) mode. Elemental analyses were performed by Schwarkopf laboratories, Woodside, NY, or Galbraith Laboratories, Knoxville, TN.

Materials. $BrCF_2CF_2I$, $ClCF_2CF_2I$, ICF_2CF_2I, $BrCF_2CF_2Br$, C_6F_5I, C_2F_5I, $(CF_3)_2CFI$, C_4F_9I, and $C_6F_{13}I$ were obtained from PCR Inc.; $ClCF_2CFClCF_2CF_2I$ was obtained from Japan Halon. $CF_2{=}CFCF_2I$ was donated by Y. Tarumi (University of Iowa). $I(CF_2)_3I$,[26] CF_3CCl_2I,[33] and $I(CF_2)_4SO_2F$[34] were prepared by reported procedures. $I(CF_2)_4I$ and $ICF_2CF_2OCF_2CF_2SO_2F$ were obtained from the Shanghai Institute of Organic Chemistry, China. $(EtO)_3P$, $(i\text{-}PrO)_3P$, $(EtO)_2POP(OEt)_2$, $Me_3COOCMe_3$, and Me_3COOH were purchased from Aldrich Chemical Company $(EtO)_3P$ and $(i\text{-}PrO)_3P$ were distilled over Na prior to use. $CF_2ClCFCl_2$ and DMF were distilled over P_2O_5 and CaH_2, respectively.

Method A. Representative Procedure for the Preparation of $(EtO)_2P(O)R_f$ *via* Photochemical Reaction of $(EtO)_2POP(OEt)_2$ and R_fI. I. $R_fP(O)(OEt)_2$ {$R_f = CF_3$, C_2F_5, $(CF_3)_2CF$, $CF_2CF{=}CF_2$, C_4F_9, C_6F_{13}, $ClCF_2CF_2$, $BrCF_2CF_2$}. Into a quartz tube (~20 mL capacity) equipped with a Teflon valve was added $(EtO)_2POP(OEt)_2$ (5.80 g, 22 mmol) under a stream of N_2, which was degassed *via* two freeze−pump−thaw cycles (liquid N_2, ~0.05 mm Hg), and R_fI (15 mmol) ($R_f = CF_3$, C_2F_5) was condensed into the tube. The Teflon valve was closed, and the tube was warmed to room temperature. [For R_fI ($R_f = (CF_3)_2CF$, $ClCF_2CF_2$, $BrCF_2CF_2$, $CF_2CF{=}CF_2$, C_4F_9, C_6F_{13}), the appropriate iodide was added *via* syringe to the tetraethylpyrophosphite under N_2 and the reaction mixture was degassed immediately]. The degassed reaction mixture was irradiated (254 nm, Rayonet photochemical reactor) at ambient temperature for 6−8 h (with CF_3I, only 4.5 h). The resultant reaction mixture from the quartz tube was transferred to a 100 mL flask equipped with a nitrogen-tee and magnetic stirbar, 15 mL of DMF was added, the flask was cooled by a salt/ice bath (−20 to −10 °C), and Me_3COOH (45 mmol) in MeOH (25 mL) was added dropwise to the stirred reaction mixture, under N_2; after complete addition, the reaction mixture was stirred for an additional hour. The resultant reaction mixture was concentrated on a rotary evaporator, the residue poured into water (~150 mL), and the crude phosphonate was separated as the lower layer, which was transferred by a pipette to CH_2Cl_2 (100 mL); the water layer was extracted with 25 mL of CH_2Cl_2. The combined CH_2Cl_2 extracts (125 mL) were dried ($MgSO_4$) and concentrated. The pure product was obtained by distillation or by column chromatography (silica gel, CH_2Cl_2/hexanes (20:80) or EtOAc/hexanes (10:90)). Boiling points and spectral data of the phosphonates are given below.

Diethyl (trifluoromethyl)phosphonate (1, $(EtO)_2P(O)CF_3$): yield 1.93 g, 63%; bp 50−52 °C/4 mm Hg (lit.[21] 65−67.5 °C (8 mm Hg)); ^{19}F NMR ($CDCl_3$) −73.3 (d, $^2J_{P,F} = 124$ Hz); $^{31}P\{^1H\}$ NMR ($CDCl_3$) −2.59 (q, $^2J_{P,F} = 124$ Hz); ^1H NMR ($CDCl_3$) 1.42 (t, 6H, $^3J_{H,H} = 7$ Hz), 4.35 (m, 4H); GC/MS (70 eV) *m/e* (% rel intensity) 207 ($M^+ + 1$, 0.2), 191 (0.8), 179 (8), 163 (11), 151 (27), 137 (36), 131 (3), 121 (7), 109 (98), 93 (39), 91 (36), 81 (100), 69 (14).

Diethyl (pentafluoroethyl)phosphonate (2, $(EtO)_2P(O)C_2F_5$): yield 2.2 g, 58%; bp 58−60 °C (5−7 mm Hg); ^{19}F NMR ($CDCl_3$) −82.0 (s, 3F), −126.13 (d, 2F, $^2J_{P,F} = 88$ Hz); $^{31}P\{^1H\}$ NMR ($CDCl_3$) 0.39 (t, $^2J_{P,F} = 88$ Hz); ^1H NMR ($CDCl_3$) 1.41 (t, 6H, $^3J_{H,H} = 7$ Hz), 4.35 (m, 4H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) 16.3 (d, $^3J_{POC,C} = 4$ Hz), 66.2 (d, $^2J_{POC} = 7$ Hz), 110.6 (qtd, overlaps), 118.5 (tdq, overlaps); GC/MS (70 eV) *m/e* (% rel intensity) 257 ($M^+ + 1$, 0.9), 241 (2), 213 (21), 201 (41), 181 (12), 137 (52), 109 (100), 93 (13), 91 (35), 81 (100), 69 (10), 65 (27); FT-IR 2987 (w), 1323 (w), 1219 (s), 1165 (m), 1123 (m), 1050 (m), 1026 (s) cm^{-1}.

Diethyl (perfluoroisopropyl)phosphonate (3, $(EtO)_2P(O)CF(CF_3)_2$): yield 2.9 g, 63%; bp 65−67 °C (7 mm Hg) (lit.[22] 70−72 °C (21 mm Hg)); ^{19}F NMR ($CDCl_3$) −72.4 (d, 6F, $^3J_{F,F} = 10$ Hz), −192.6 (d heptets, 1F, $^2J_{P,F} = 71$ Hz, $^3J_{F,F} = 10$ Hz); $^{31}P\{^1H\}$ NMR ($CDCl_3$) 2.44 (d, $^2J_{P,F} = 71$ Hz); ^1H NMR ($CDCl_3$) 1.41 (t, 6H, $^3J_{H,H} = 7$ Hz), 4.37 (m, 4H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) 16.32 (d, $^3J_{POC,C} = 5$ Hz), 66.41 (d, $^2J_{PO,C} = 7$ Hz), 89.90 (ddh, $^1J_{C,F} = 238$ Hz, $^1J_{P,C} = 160$ Hz, $^2J_{C,F} = 34$ Hz), 120.45 (qd, $^1J_{C,F} = 287$ Hz, $^2J_{C,F} = 25$ Hz); GC/MS (70 eV) *m/e* (% rel intensity) 307 ($M^+ + 1$, 2), 291 (1), 279 (26), 277 (10), 263 (16), 251 (70), 233 (15), 231 (18), 150 (5), 137 (75), 131 (45), 109 (100), 93 (38), 91 (39), 81 (85), 69 (15), 65 (43); FT-IR 2987 (w), 1300 (m), 1285 (m), 1267 (m), 1228 (s), 1166 (w), 1054 (m), 1026 (s) cm^{-1}.

Diethyl (perfluorobutyl)phosphonate (4, $(EtO)_2P(O)C_4F_9$): yield 3.9 g, 69%; bp 64−65 °C (0.5 mm Hg) (lit.[22] 52−53 °C (7 mm Hg)); ^{19}F NMR ($CDCl_3$) -81.5 (m, 3F), −121.9 (m, 2F), −122.6 (dt, 2F, $^2J_{P,F} = 90$ Hz), −126.4 (t, 2F); $^{31}P\{^1H\}$ NMR ($CDCl_3$) 0.37 (t, $^2J_{P,F} = 90$ Hz); ^1H NMR ($CDCl_3$) 1.41 (t, 6H, $^3J_{H,H} = 7$ Hz), 4.37 (m, 4H); GC/MS (70 eV) *m/e* (% relative intensity) 357 ($M^+ + 1$, 0.7), 356 (M^+, 0.1), 327 (10), 301 (43), 281 (9), 137 (65), 131 (10), 109 (100), 93 (15), 91 (27), 81 (56), 69 (10), 65 (16); FT-IR: 2987 (w), 1241 (s), 1210 (m), 1150 (m), 1123 (m), 1045 (m), 1024 (s) cm^{-1}.

Diethyl (perfluorohexyl)phosphonate (5, $(EtO)_2P(O)C_6F_{13}$): yield 5.4 g, 79%; bp 68−70 °C (0.7 mm Hg) (lit.[22] 58−60 °C (1.5 mm Hg)); ^{19}F NMR ($CDCl_3$) −81.4 (t, 3F, $J_{F,F} = 10$ Hz), −120.8 (brs, 2F), −122.3 (brs, 2F), −121.1 to −121.9 (overlaps, 8F), −126.6 (brs, 2F); $^{31}P\{^1H\}$ NMR ($CDCl_3$) 0.81 (t, $^2J_{P,F} = 90$ Hz); ^1H NMR ($CDCl_3$) 1.41 (t, 6H, $^3J_{H,H} = 7$ Hz), 4.37 (m, 4H); GC/MS (70 eV) *m/e* (% rel intensity) 456 (M^+, 0.2), 430 (2), 402 (12), 381 (6), 231 (2), 181 (4), 137 (77), 109 (54), 93 (35), 91 (54), 81 (86), 69 (23), 65 (31); FT-IR 2987 (w), 1293 (m), 1241 (s), 1210 (m), 1149 (m), 1045 (w), 1024 (s) cm^{-1}.

Diethyl (pentafluorophenyl)phosphonate (11, $(EtO)_2P(O)C_6F_5$): yield 1.05 g, 35%; bp 66−67 °C (0.05 mm Hg) (lit.[21] 146−156 °C (8 mm Hg)); ^{19}F, $^{31}P\{^1H\}$, and ^1H NMR and IR data same as those reported;[21] GC/MS (70 eV) *m/e* (% rel intensity) 304 (M^+, 1), 289 (2), 277 (14), 259 (9), 257 (16), 256 (42), 249 (100), 241 (12), 231 (62), 184 (19), 176 (24), 168 (20), 167 (12), 137 (8), 93 (6), 81 (13), 67 (8), 65 (29).

Diethyl (perfluoroallyl)phosphonate (6, $(EtO)_2P(O)CF_2CF{=}CF_2$): yield 2.4 g, 59%; bp 45−46 °C (0.8 mm Hg) (lit.[35] 36−40 °C (0.03 mm Hg)); ^{19}F NMR ($CDCl_3$) −91 (m, 1F), −107.3 (m, 1F), −117.3 (dm, 2F), −187.7 (m, 1F); $^{31}P\{^1H\}$ NMR ($CDCl_3$) 3.4 (tm, $^2J_{P,F} = 98$ Hz); ^1H NMR ($CDCl_3$) 1.41 (t, 6H, $^3J_{H,H} = 7$ Hz), 4.34 (m, 4H); GC/MS (70 eV) *m/e* (% rel intensity) 269 ($M^+ + 1$, 0.9), 240 (9), 225 (30, 212 (55), 193 (11), 173 (3), 137 (18), 131 (57), 109 (84), 91 (35), 81 (100), 69 (10), 65 (16); FT-IR 2978 (w), 1784 (m), 1346 (m), 1295 (s), 1176 (m), 1097 (m), 1047 (m), 1024 (s), 806 (m) cm^{-1}.

Diethyl (2-bromotetrafluoroethyl)phosphonate (7, $(EtO)_2P(O)CF_2CF_2Br$): yield 3.8 g, 80%; bp 40−45 °C (0.3 mm Hg); ^{19}F NMR ($CDCl_3$) −62.4 (m, 2F), −116.1 (dt, 2F, $^2J_{P,F} = 93$ Hz, $^3J_{F,F} = 5$ Hz); $^{31}P\{^1H\}$ NMR ($CDCl_3$) −0.48 (tt, $^2J_{P,F} = 93$ Hz, $^3J_{P,F} = 4$ Hz; ^1H NMR

(33) (a) Lang, R. W. *Helv. Chim. Acta* **1988**, *71*, 369. (b) Unpublished work of J. MacNeil, University of Iowa.

(34) Qiu, W.; Burton, D. J. *J. Fluorine Chem.* **1993**, *60*, 93.

(35) Sprague, L. G. Ph.D. Thesis, University of Iowa, 1984, p 276.

($CDCl_3$) 1.41 (t, 6H), 4.40 (m, 4H), $^3J_{H,H} \simeq J_{P,H} \approx 7$ Hz; $^{13}C\{^1H\}$ NMR ($CDCl_3$) 16.31 (d, $^3J_{POC,C} = 5$Hz), 66.07 (d, $^2J_{POC} = 7$ Hz), 111.52 (tdt, $^1J_{C,F} = 276$ Hz, $^1J_{P,C} = 204$ Hz, $^2J_{C,F} = 37$ Hz), 117.20 (ttd, $^1J_{C,F} = 310$ Hz, $^2J_{C,F} = 36$ Hz, $^2J_{P,C} = 19$ Hz); GC/MS *m/e* (% rel intensity) 319/317 ($M^+ + 1$, 1), 303 (1), 289 (24), 273 (9), 263 (31), 243 (21), 209 (27), 193 (15), 181 (50), 137 (82), 109 (100), 91 (20), 81 (66), 65 (13); FT-IR 2987, 2935, 1444, 1395, 1373, 1292, 1228, 1165, 1125, 1081,1025, 985, 895, 821, 779, 769, 586, 552 cm^{-1}. Anal. Calcd. for $C_6H_{10}O_3PF_4Br$: C, 22.73; H, 3.18; P, 9.70; F, 23.97; Br, 25.21. Found: C, 23.09; H, 3.29; P, 9.17; F, 24.49; Br, 25.27.

Diethyl (2-chlorotetrafluoroethyl)phosphonate (8, $(EtO)_2P(O)CF_2CF_2Cl$): yield 3.1 g, 75%; bp 50−60 °C (0.8 mm Hg); ^{19}F NMR ($CDCl_3$) −67.7 (m, 2F), −119.3 (dt, 2F, $^2J_{P,F} = 90$ Hz, $^3J_{F,F} = 5$ Hz); $^{31}P\{^1H\}$ NMR ($CDCl_3$) 0.23 (tt, $^2J_{P,F} = 91$ Hz, $^3J_{P,F} = 4$ Hz); ^1H NMR ($CDCl_3$) 1.41 (t, 6H, $^3J_{H,H} \approx {}^3J_{P,H} = 7$ Hz), 4.36 (m, 4H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) 16.31 (d, $^3J_{POC,C} = 5$ Hz), 66.02 (d, $^2J_{POC} = 7$ Hz), 111.55 (tdt, $^1J_{C,F} = 276$ Hz, $^1J_{P,C} = 206$ Hz, $^2J_{C,F} = 39$ Hz), 123.18 (ttd, $^1J_{C,F} = 298$ Hz, $^2J_{C,F} = 39$ Hz, $^2J_{P,C} = 21$ Hz); GC/MS *m/e* (% rel intensity) (no M^+) 247 (1), 245 (6), 231 (2), 229 (6), 219 (6), 217 (18), 209 (4), 199 (9), 181 (24), 137 (80), 109 (100), 100 (17), 93 (18), 81 (92), 67 (13), 65 (29); FT-IR 2986, 2934, 1444, 1395, 1373, 1292, 1242, 1166, 1123, 1091, 1025, 985, 964, 922, 847, 836, 807, 796, 784, 776, 766, 756, 749, 741 cm^{-1}. Anal. Calcd. for $C_6H_{10}O_3PF_4Cl$: C, 26.44; H, 3.70; P, 11.36; F, 27.88; Cl, 13.00. Found: C, 26.51; H, 3.65; P, 10.82; F, 27.77; Cl, 12.86.

II. $R_fP(O)(OEt)_2$ {$R_f = (CF_2)_4SO_2F$, $ClCF_2CFClCF_2CF_2$, $CF_2CF_2OCF_2CF_2SO_2F$, C_6F_5}. A degassed mixture of $(EtO)_2POP(OEt)_2$ (15 mmol) and appropriate R_fI (10 mmol) was irradiated (254 nm) at ambient temperature (in the case of C_6F_5I, 300 nm) for 6−8 h. [For the preparation of $FSO_2(CF_2)_4P(O)(OEt)_2$, a degassed mixture of $I(CF_2)4SO_2F$ (7.8 mmol) and $(EtO)_2POP(OEt)_2$ (12 mmol) was irradiated for 6−8 h]. After of 10 mL of DMF was added to the reaction mixture, oxidation {with Me_3COOH (30 mmol) in MeOH (20 mL)} and workup were performed the same way as outlined above (method A.I). Phosphonates were isolated by distillation under reduced pressure.

Diethyl (3,4-dichloro-1,1,2,2,3,4,4-heptafluorobutyl)phosphonate (12, $(EtO)_2P(O)CF_2CF_2CFClCF_2Cl$): yield 3.0 g, 72%; bp 55−57 °C (0.05−0.02 mm Hg); ^{19}F NMR ($CDCl_3$) −63.9 (d, 2F, $^2J_{F,F} = 7$ Hz), −112.9 (s, 2F), −119.6 (AB pattern, 2F, $^1J_{F,F} = 336$ Hz, $^2J_{P,F} = 91$ Hz), −131.3 (s, 1F); $^{31}P\{^1H\}$ NMR ($CDCl_3$) 1.03 (t, $^2J_{P,F} = 91$ Hz); ^1H NMR ($CDCl_3$) 1.41 (t, 6H, $^3J_{H,H} = 7$ Hz), 4.40 (m, 4H); GC/MS (70 eV) *m/e* (% rel intensity) 391 ($M^+ + 1$, ^{37}Cl, 0.3), 389 (M^++1, ^{35}Cl, 0.7), 390 (M^+, 0.1), (388 (M^+, 0.1), 375 (0.5), 373 (9), 363 (3), 361 (7), 359 (5), 347 (3), 345 (5), 335 (10), 333 (15), 299 (5), 297 (16), 137 (84), 109 (100), 93 (36), 91 (58), 81 (92), 69 (15); FT-IR 2986 (w), 1295 (m), 1295 (m), 1184 (s), 1162 (m), 1131 (s), 1051 (s), 1024 (s) cm^{-1}.

Diethyl (2-(2-fluorosulfonyltetrafluoroethoxy)tetrafluoroethyl)-phosphonate (13, $(EtO)_2P(O)CF_2CF_2OCF_2CF_2SO_2F$): yield 2.47 g, 57%; bp 38−40 °C (0.05 mm Hg); ^{19}F NMR ($CDCl_3$) +45.4 (brs, 1F), −82.2 (brs, 2F), −83.6 (m, 2F), −112.4 (s, 2F), −125.1 (d, 2F, $^2J_{P,F} = 91$ Hz); $^{31}P\{^1H\}$ NMR ($CDCl_3$) -0.41 (t, $^2J_{P,F} = 90$ Hz); ^1H NMR ($CDCl_3$) 1.41 (t, 6H, $^3J_{H,H} = 7$ Hz), 4.37 (m, 4H); GC/MS *m/e* (% rel intensity) 437 ($M^+ + 1$, 0.1), 421 (0.2), 409 (1), 381 (4), 297 (8), 199 (5), 181 (13), 137 (57), 119 (8), 109 (100), 100 (25), 93 (15), 91 (27), 81 (73), 69 (11), 65 (23); FT-IR 2987 (w), 1462 (s), 1297 (m), 1244 (m), 1208 (s), 1151 (vs), 1125 (m), 1025 (s) cm^{-1}.

Diethyl (4-(fluorosulfonyl)perfluorobutyl)phosphonate (14, $(EtO)_2P(O)(CF_2)_4SO_2F$): yield 2.1 g, 64%; bp 48−52 °C (0.01 mm Hg); ^{19}F NMR ($CDCl_3$) +45.9 (d, 1F), −107.9 (s, 2F), −120.3 (s, 2F), −120.5 (s, 2F), −122.5 (dt, 2F, $^2J_{P,F} = 90$ Hz); $^{31}P\{^1H\}$ NMR ($CDCl_3$) 0.13 (t, $^2J_{P,F} = 91$ Hz); ^1H NMR ($CDCl_3$) 1.42 (t, 6H, $^3J_{H,H} = 7$ Hz), 4.39 (m, 4H); GC/MS *m/e* (% rel intensity) 421 ($M^+ + 1$, 0.1), 365 (3), 281 (3), 181 (1), 137 (40), 131 (11), 109 (100), 100 (12), 93 (16), 91 (25), 81 (47), 69 (7); FT-IR 2987 (w), 1461 (s), 1294 (m), 1238 (m), 1209 (s), 1146 (s), 1049 (m), 1024 (vs) cm^{-1}.

1,3-Diiodoperfluoropropane.[26] Perfluoroglutaryl chloride (75.0 g, 0.271 mol) and potassium iodide (120.0 g, 0.723 mol) were heated, with constant mechanical stirring, in a 300 mL stainless steel pressure reactor (Parr reactor) for 6.0 h at 200 °C and 900−1000 psi (autogenous pressure). The Parr reactor was then cooled to room temperature, the valve was opened to release the CO formed (*Caution! in a well-ventilated fume hood*), and the contents were poured into 200 mL cold water. The product, 1,3-diiodo-1,1,2,2,3,3-hexafluoropropane, was separated in the lower layer which was taken up in 100 mL of Et_2O, washed with 50 mL of H_2O, dried ($MgSO_4$), and distilled at 125−132 °C to give 74.6 g (68% yield) of $ICF_2CF_2CF_2I$; ^{19}F NMR ($CDCl_3$) −58.0 (t, 4F) and −105.2 (p, 2F) ppm, $^3J_{F,F} = 5$ Hz; GC/MS 404 (M^+); GLPC purity 100%.

III. $R_fP(O)(OEt)_2$ {$R_f = I(CF_2)_3$, $I(CF_2)_4$}. Similarly, a degassed mixture of diodide (12 mmol) and $(EtO)_2POP(OEt)_2$ (10 mmol) was irradiated (254 nm) for 4 h, oxidized with Me_3COOH (20 mmol) in MeOH (15 mL), and worked up (as given in method A.I); phosphonates were purified by column chromatography (silica gel, CH_2Cl_2/hexanes (20:80) or EtOAc/hexanes (10:90)).

Diethyl (3-iodohexafluoropropyl)phosphonate (9, $(EtO)_2P(O)CF_2CF_2CF_2I$): yield 1.53 g, 37%; bp 95−100 °C (0.5 mm Hg); ^{19}F NMR ($CDCl_3$) −58.7 (m, 2F), −120.7 (d, 2F), −121.2 (dt, 2F, $^2J_{P,F} = 92$ Hz, $^4J_{F,F} = 15$ Hz); $^{31}P\{^1H\}$ NMR ($CDCl_3$) 0.32 (tt, $^2J_{P,F} = 92$ Hz, $^3J_{P,F} = 5$ Hz); ^1H NMR ($CDCl_3$) 1.42 (t, $^3J_{H,H} = 7$ Hz), 4.30 (m, 4H); GC/MS *m/e* (% rel intensity) 415 ($M^+ + 1$, 0.2), 399 (0.2), 385 (2), 359 (3), 341 (5), 259 (14), 231 (66), 211 (6), 177 (14), 137 (56), 109 (100), 93 (16), 91 (35), 81 (83), 69 (11), 65 (25); FT-IR 2987 (w), 1294 (m), 1185 (s), 1107 (s), 1050 (m), 1026 (vs) cm^{-1}. Anal. Calcd. for $C_7H_{10}O_3F_6PI$: C, 20.30; H, 2.43; F, 27.53; P, 7.48; I, 30.65. Found: C, 20.00; H, 2.59; F, 27.39; P, 8.20; I, 29.10.

Diethyl (4-iodooctafluorobutyl)phosphonate (10, $(EtO)_2P(O)CF_2CF_2CF_2CF_2I$): yield 1.61 g, 35%; bp 68−70 °C (0.01 mm Hg); ^{19}F NMR ($CDCl_3$) −59.7 (m, 2F), −113.4 (m, 2F), −119.8 (m, 2F), −122.1 (dt, 2F, $^2J_{P,F} = 90$ Hz); $^{31}P\{^1H\}$ NMR ($CDCl_3$) −0.16 (t); ^1H NMR ($CDCl_3$) 1.40 (t, 6H, $^3J_{H,H} = 7$ Hz), 4.35 (m, 4H); GC/MS *m/e* (% rel intensity) 465 ($M^+ + 1$, 0.2), 435 (0.3), 421 (0.2), 337 (0.2), 309 (2), 281 (12), 208 (3), 177 (5), 137 (74), 109 (100), 100 (14), 93 (20), 91 (36), 81 (88), 69 (15), 65 (31); FT-IR 2987 (w), 1289 (m), 1194 (vs), 1148 (m), 1131 (vs), 1120 (m), 1051 (m), 1025 (vs) cm^{-1}.

Method B. Thermally-Induced Radical Reactions. $(EtO)_2P(O)CF_2CF_2Br$ (7). $(EtO)_2POP(OEt)_2$ (11.61 g, 45 mmol), $CFCl_2CF_2Cl$ (40 mL), $BrCF_2CF_2I$ (9.24g, 30 mmol), and $Me_3COOCMe_3$ (3.04 g, 20mmol) were introduced sequentially into a 400 mL capacity hard glass Rotaflo tube equipped with Teflon stopcock and magnetic stir bar, under nitrogen. The reaction mixture was degassed (∼0.005 mm Hg) *via* two freeze−pump−thaw (liquid N_2) cycles and brought to room temperature. The stirred reaction mixture was then heated (*Caution! the reaction should be carried out in a well-ventilated fume-hood behind a safety shield*) slowly to 125−130 °C in an oil bath and maintained at this temperature for 3.5 h, cooled to room temperature, and transferred to a 250 mL flask placed in an ice/salt bath. To the resultant reaction mixture, Me_3COOH (8.10 g, 90 mmol) in MeOH (40 mL) was added dropwise *via* an addition funnel, over a period of 20 min with constant magnetic stirring. After 1 h of stirring, the reaction mixture was concentrated on a rotary evaporator, and the residue was extracted with $CHCl_3$ (200 mL) and washed successively with water (2 × 50 mL), saturated $NaHCO_3$ (5 mL), saturated $NaHSO_3$ (5 mL), and brine (5 mL). The $CHCl_3$ layer was separated, dried ($MgSO_4$), and concentrated on a rotary evaporator. The residue was chromatographed (silica gel column, eluent CH_2Cl_2/hexanes (15:85)). The crude phosphonate was distilled *via* a short-path distillation apparatus. $(EtO)_2P(O)CF_2CF_2Br$ (5.80 g, 62% yield) was collected at 42−45 °C (0.3 mm Hg).

$(C_2H_5O)_2P(O)CF_2CF_2Cl$ (8). Similarly, $(C_2H_5O)_2P(O)CF_2CF_2Cl$ was prepared from $ClCF_2CF_2I$ and $(EtO)_2POP(OEt)_2$, as described above for **7**. The title compound was obtained in 53% yield (4.30 g) on distillation (50−60 °C (0.8 mm Hg)) *via* a short-path distillation apparatus.

Method C. Reaction CF_3CCl_2I with $(EtO)_2POP(OEt)_2$. Diethyl (1,1-dichloro-2,2,2-trifluoroethyl)phosphonate (15, $(EtO)_2P(O)CCl_2CF_3$). In a 25 mL round-bottomed flask equipped with a septum port, nitrogen-tee, and a magnetic stirbar was added 15 mmol of $(EtO)_2POP(OEt)_2$. Then, 10 mmol CF_3CCl_2I was added dropwise (an immediate exothermic reaction was observed), and the reaction mixture was stirred for 30 min. To the resultant reaction mixture, 10 mL of DMF was added, and the oxidized by Me_3COOH (30 mmol) in MeOH (20 mL) and worked up as given in method A.I. For **12**: yield 1.5 g, 52 %; bp 52−55 °C (0.3 mm Hg); ^{19}F NMR ($CDCl_3$) −74.2 (brs); $^{31}P\{^1H\}$ NMR ($CDCl_3$) 4.90 (s); ^1H NMR ($CDCl_3$) 1.41 (t, 6H, $^3J_{H,H}$

= 7 Hz), 4.40 (m, 4H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) 16.31 (d, $^3J_{POC,C}$ = 6 Hz), 66.07 (d, $^2J_{POC}$ = 7 Hz), 76.10 (dq, $^1J_{P,C}$ = 166Hz, $^2J_{C,F}$ = 37 Hz), 121.70 (qd, $^1J_{C,F}$ = 283 Hz, $^2J_{P,C}$ = 6 Hz); GC/MS (70 eV) *m/e* (% rel intensity) 289 (M^+ + 1, 0.2), 273 (0.2), 259 (1), 240 (2), 151 (4), 137 (36), 132 (17), 109 (100), 93 (11), 91 (27), 81 (63); FTIR 2986 (w), 1286 (m), 1242 (m), 1200 (s), 1164 (w), 1054 (m), 1027 (s) cm^{-1}.

Method D. Photochemical Reaction of $BrCF_2CF_2I$ with Trialkylphosphites. $(i\text{-}C_3H_7O)_2P(O)CF_2CF_2I$ (17). (i-$C_3H_7O)_3P$ (12.49 g, 60 mmol), which was freshly distilled over sodium, was introduced *via* syringe to a quartz Rotaflo tube (~30 mL capacity) equipped with a Teflon stopcock, under nitrogen. The tube was cooled to −196 °C and evacuated (~0.05 mm Hg), and $BrCF_2CF_2I$ (9.24 g, 30 mmol) was condensed on to the (i-$C_3H_7O)_3P$. The Rotaflo tube was then sealed and brought to room temperature. The reaction mixture was irradiated at 254 nm (Rayonet photochemical apparatus) for 3.5 h at ambient temperature and concentrated under reduced pressure (0.1−0.05 mm Hg). The residue was extracted with 150 mL of $CHCl_3$, washed with water (50 mL) and brine (25 mL), concentrated on a rotary evaporator, and chromatographed (silica gel column, eluent CH_2Cl_2/hexanes (20:80)). The crude phosphonate was distilled at 55−65 °C (0.05−0.02 mm Hg), using a short-path distillation apparatus, to afford the title compound (5.60 g, 48% yield). Spectral data: ^{19}F NMR ($CDCl_3$) −56.2 (m, 2F), −111.5 (dt, 2F, $^2J_{P,F}$ = 96 Hz, $^3J_{P,F}$ = 5 Hz, $^3J_{F,F}$ = 8 Hz; $^{31}P\{^1H\}$ NMR ($CDCl_3$) −4.36 (tt); ^1H NMR ($CDCl_3$) 1.40 (d, 6H), 1.38 (d, 6H), 4.91 (m, 2H, $^3J_{H,H}$ = 6 Hz). $^{13}C\{^1H\}$ ($CDCl_3$) 23.50 (d, $^3J_{POC,C}$ = 6 Hz) 24.15 (d, $^3J_{POC,C}$ = 3 Hz), 75.49 (d, $^2J_{PO,C}$ = 6 Hz), 97.48 (ttd, $^1J_{C,F}$ = 317 Hz, $^2J_{C,F}$ = 40 Hz, $^2J_{P,C}$ = 15 Hz), 111.13 (tdt, $^1J_{C,F}$ = 274 Hz, $^1J_{P,C}$ = 203 Hz, $^2J_{C,F}$ = 36 Hz); GC/MS *m/e* (% rel intensity) 392 (M^+, 0.4), 377 (1), 349 (3), 355 (69), 309 (31), 289 (16), 223 (64), 208 (3), 191 (3), 181 (100), 165 (16), 127 (6), 123 (78), 100 (7), 91 (3), 81 (14), 65 (9); FT-IR 2986, 2941, 1389, 1378, 1287, 1180, 1149, 1118, 1103, 1070, 1006 cm^{-1}. Anal. Calcd. for $C_8H_{14}O_3PF_4I$: C, 24.50; H, 3.60; P, 7.90; F, 19.38; I, 32.37. Found: C, 24.80; H, 3.76; P, 7.89; F,19.54; I, 32.55.

$(EtO)_2P(O)CF_2CF_2I$ (16). Similarly, a mixture of $(EtO)_3P$ (9.96 g, 60 mmol) and $BrCF_2CF_2I$ (9.24 g, 30 mmol) was irradiated at 254 nm for 2.5 h at ambient temperature and worked-up as described above for the isopropyl analogue **17**. $(EtO)_2P(O)CF_2CF_2I$ (4.6 g, 42%) was collected at 55−65 °C (0.10 mm Hg) *via* distillation using a short-path distillation apparatus. For **16**: ^{19}F NMR ($CDCl_3$) −57.20 (m, 2F), −111.15 (dt, 2F), $^2J_{P,F}$ = 95 Hz, $^3J_{P,F}$ = 5 Hz $^3J_{F,F}$ = 7 Hz; $^{31}P\{^1H\}$ NMR ($CDCl_3$) −3.0 (tt); ^1H NMR ($CDCl_3$) 1.40 (t, 6^1H), 4.35 (p, (dq overlaps), 4H), $^3J_{H,H} \approx {}^3J_{P,H}$ = 7 Hz. $^{13}C\{^1H\}$ NMR ($CDCl_3$) 16.2 (d, $^3J_{POC,C}$ = 5 Hz), 65.9 (d, $^2J_{PO,C}$ = 6 Hz), 97.3 (ttd, $^1J_{C,F}$ = 317 Hz, $^2J_{C,F}$ = 37 Hz, $^2J_{P,C}$ = 14 Hz), 111.35 (tdt, $^1J_{C,F}$ = 273 Hz, $^1J_{P,C}$ = 201 Hz, $^2J_{C,F}$ = 37 Hz); GC/MS *m/e* (% rel intensity) 364 (M^+, 3), 336 (4), 322 (3), 291 (6), 209 (5), 181 (5), 138 (5), 137 (66), 131 (20), 129 (7), 127 (3), 121 (7), 119 (7), 111 (6), 110 (5), 109 (100), 100 (11), 93 (22), 91 (25), 81 (81), 69 (15), 65 (29), 51 (3); FT-IR 2987, 2934, 2915, 1443,1395, 1372, 1290, 1225, 1210, 1148, 1121, 1071, 1023 cm^{-1}. Anal. Calcd. for $C_6H_{10}O_3PF_4I$: C, 19.80; H, 2.77; P, 8.51; F, 20.88; I, 34.86. Found: C, 19.78; H, 2.67; P, 8.23; F, 21.10; I, 35.27.

Acknowledgment. We thank the National Science Foundation for generous support of this work.

JA971345T