The Synthesis of Phosphonate Ester Containing Fluorinated Vinyl Ethers

Scot D. Pedersen, Weiming Qiu, Zai-Ming Qiu, Stefan V. Kotov, and Donald J. Burton*

Department of Chemistry, University of Iowa, Iowa City, Iowa 52242

Received June 10, 1996[⊗]

Three novel perfluorovinyl ethers containing phosphonate ester groups, diethyl 1,1,2,2,3,3,5,6,6-nonafluoro-4-oxa-5-hexenylphosphonate, $(EtO)_2P(O)(CF_2)_3OCF{=}CF_2$ (**1**), diethyl 1,1,2,2,4,5,5-heptafluoro-3-oxa-4-pentenylphosphonate, $(EtO)_2P(O)(CF_2)_2OCF{=}CF_2$ (**2**), and diethyl 1,1,2,2,4,5,5,7,8,8-decafluoro-4-trifluoromethyl-3,6-dioxa-7-octenylphosphonate, $CF_2{=}CFOCF_2CF(CF_3)O(CF_2)_2P(O)(OEt)_2$ (**3**), have been synthesized. Perfluorovinyl ethers **1** and **2** were synthesized from methyl 4-trifluoroethenoxy-2,2,3,3,4,4-hexafluorobutanoate and methyl 3-trifluoroethenoxy-2,2,3,3-tetrafluoropropanoate, respectively, while perfluorovinyl ether **3** was synthesized either from 5-trifluoroethenoxy-4-trifluoromethyl-3-oxa-1,1,2,2,4,5,5-heptafluoropentylsulfonyl fluoride or methyl 6-trifluoroethenoxy-5-trifluoromethyl-4-oxa-2,2,3,3,5,6,6-heptafluorohexanoate. The carboxylate esters were converted to the corresponding fluoroalkyl iodides *via* a free-radical iododecarboxylation. The sulfonyl fluoride was converted to its corresponding fluoroalkyl iodide *via* iododesulfination. The intermediate iodides were found to be useful precursors for the incorporation of the phosphonic ester groups *via* a photoreaction with tetraethyl pyrophosphite to produce diethyl fluorophosphonites. The diethyl fluorophosphonites were oxidized to the desired phosphonates, **1**, **2**, and **3**, utilizing hydrogen peroxide as the oxidant. Moderate to good overall yields of perfluorovinyl ethers **1**−**3** have been achieved.

Introduction

In the past 2 decades, there has been a major research effort in the area of ion-containing copolymers (ionomers). Specifically, those ionomers that are based on poly(tetrafluoroethylene) are of great interest as membranes in chloralkali cells and fuel cells. The vast majority of the research done to date has concentrated on poly(tetrafluoroethylene)-based membranes that contain either sulfonate[1] or carboxylate[2] groups or a combination of sulfonate and carboxylate[3] groups as the ionic species. The literature lacks studies on, and methodologies for, the preparation of membranes that utilize either phosphonic acid groups or quarternary alcohol groups due to the difficulties in monomer production.[4] However, it has been suggested that perfluorinated phosphonic acids may be useful as substitutes for, or additives to, H_3PO_4 electrolytes in fuel cells.[5] The above discussions led us to explore the production of possible phosphonate ester containing monomers for copolymerization with tetrafluoroethylene.

The synthesis of phosphonic acid containing monomers, or organophosphorous compounds in general, must involve at some stage the formation of a carbon−phosphorus linkage. The most widely recognized method for the generation of the carbon−phosphorus bond is the Arbuzov[6] reaction, where trialkyl phosphites react with alkyl halides to form quasi-phosphonium intermediates which immediately dealkylate to generate alkylphosphonates (Scheme 1). A modification of the Arbuzov reaction was reported by Michaelis and Becker.[7] The Michaelis−Becker reaction involves attack of a dialkyl phosphite anion on an alkyl halide to yield alkanephosphonates by nucleophilic substitution (Scheme 2). The general scope and applicability of the Arbuzov and Michaelis−Becker syntheses, however, cannot be generally extended to fluorinated alkyl halides. The strong electron-withdrawing ability of the fluorine atom causes the site of nucleophilic attack to be the halogen rather than the carbon.

Fluoropoly(halomethanes) have been reported to undergo Arbuzov-type reactions. Burton *et al.*[8] reported that some difluorodihalomethanes yield Arbuzov products in the presence of trialkyl phosphites (Scheme 3). It has been suggested,[8] however, that the mechanism for the formation of difluorohalomethylphosphonates occurs *via* trapping of the corresponding difluorocarbene. Generation of difluorocarbene presumably occurs *via* halophilic attack of the trialkyl phosphite on the difluorodihalomethanes. Fluorodihalomethanephosphonates have also been synthesized when fluorotrihalomethanes were reacted with trialkyl phosphites (Scheme 3). However, the mechanism for the formation of fluorodihalomethanephosphonates does not proceed *via* the direct nucleophilic attack on the carbon center of the fluorotrihalomethanes.[8] Longer chain fluorinated alkyl halides, however, have not been shown to undergo such Arbuzov-like reactions.

It has also been reported[9] that iodotrifluoromethane and iodopentafluorobenzene react with triethyl phosphite when irradiated with 350 nm light (Scheme 4) to yield diethyl trifluoromethylphosphonate and diethyl pentafluorophenylphosphonate in 51% and 32% yield. However, other perfluoroalkyl halides have not been reported to undergo similar reactions.

[⊗] Abstract published in *Advance ACS Abstracts,* October 15, 1996.

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(2) Seko, M. (to Asahi Chemical Ind. Co., Ltd) U.S. Patent 4 178 218, 1979; *Chem. Abstr.* **1976**, *84*, 23757d.

(3) Molnar, C. J.; Price, E. H.; Resnick, P. R. (to E. I. du Pont de Nemours and Co.) U.S. Patent 4 176 215, 1979; *Chem. Abstr.* **1980**, *92*, 66849q.

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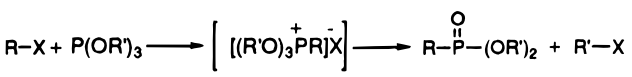
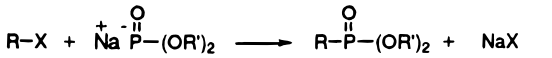
(9) Flynn, R. M.; Burton, D. J. *Synthesis* **1979**, 615.

S0022-3263(96)01086-9 CCC: $12.00

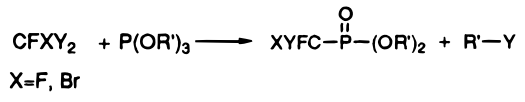
Scheme 1. The Arbuzov Reaction



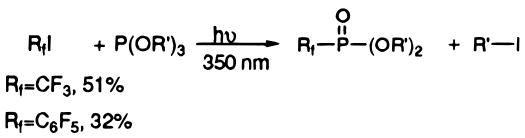
Scheme 2. The Michaelius–Becker Reaction



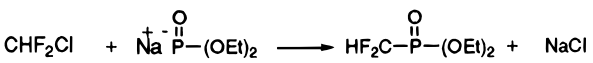
Scheme 3. Reaction of Trialkyl Phosphites with Perhalomethanes



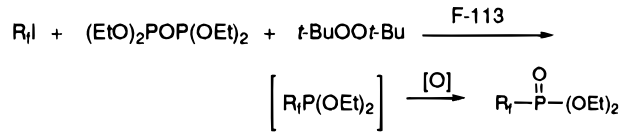
Scheme 4. Reaction of Trialkyl Phosphites with Perfluoroalkyl Iodides



Scheme 5. Reaction of Sodium Dialkyl Phosphite with Chlorodifluoromethane



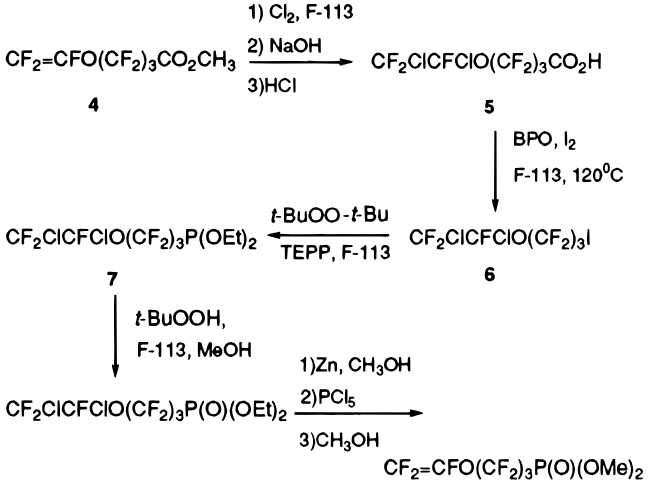
Scheme 6. Free-Radical Reaction of Perfluoroalkyl Iodides with Tetraethyl Pyrophosphite



Soborovskii and Baiva[10] have reported that difluoromethylphosphonates can be prepared by the reaction of chlorodifluoromethane with sodium dialkyl phosphite (Scheme 5). This reaction proceeds presumably *via* the generation and subsequent trapping of difluorocarbene.[11] This synthetic method suffers the same shortcomings as described above, specifically, it is not a general approach to a wide variety of fluorinated phosphonates.

In 1981, Kato and Yamabe[12] reported the synthesis of perfluoroalkanephosphonates from the corresponding perfluoroalkyl iodides *via* the phosphonites (Scheme 6). Thermal decomposition of di-*tert*-butyl peroxide leads to the abstraction of an iodine atom from the perfluoroalkyl iodide to produce the reactive perfluoroalkyl radical. The perfluoroalkyl radical, then, reacts with tetraethyl pyrophosphite resulting in perfluoroalkylphosphonite. Simple oxidation with *tert*-butyl hydroperoxide provides the desired perfluoroalkylphosphonates. Kato and Yamabe applied this strategy to the preparation of a perfluorovinyl ether containing a phosphonate ester group (Scheme 7).[13] During their synthesis, Kato *et al.* protect the trifluorovinyl ether functionality of a carboxylate

Scheme 7. Synthesis of a Fluorinated Vinyl Ether Containing a Phosphonate Ester Group



Scheme 8. Photoreaction of Perfluoroalkyl Iodides with Tetraethyl Pyrophosphite

ester **4** containing a trifluorovinyl ether group using excess chlorine. Subsequent synthetic steps convert the ester **4** to the dimethyl phosphonate. This synthetic methodology suffers severely due to synchronous dealkylation of the phosphonate upon removal of the chlorine protection from the trifluorovinyl ether function. Attempts to reproduce this work in our laboratory resulted in low yields due to the difficult and cumbersome distillation of the intermediate phosphoryl chlorides.

Recent work in our laboratories has provided an improvement over the procedure of Kato and Yamabe.[12,13] Nair and Burton[14] reported in 1994 that perfluoroalkyl iodides, including 1,3-, 1,4-, and 1,6-diiodides, reacted with tetraethyl pyrophosphite under ultraviolet irradiation to afford, in good to excellent yields, the corresponding perfluoroalkylphosphonites and bisphosphonites, which could be easily oxidized to the corresponding perfluoroalkylphosphonates and bisphosphonates (Scheme 8). The much milder reaction temperatures should allow for more complex perfluoroalkyl iodides to be employed in the photochemical reaction versus the higher temperature Kato–Yammabe method.

Herein, we report the complete synthesis of three novel fluoroalkylphosphonates containing the trifluorovinyl ether group.[15] These phosphonates have been synthesized for co- and ter-polymerization with tetrafluoroethylene and perfluoropropyl vinyl ether to examine the structural and electrochemical properties of the resulting ionomers.[16] These fluoroalkylphosphonates provide a reasonable method for the incorporation of phosphonic acid groups into poly(tetrafluoroethylene)-based membranes.

(10) Soborovskii, L. Z.; Baiva, N. F. *Zh. Obshch. Khim.* **1959**, *29*, 1144.

(11) Flynn, R. M. Ph.D. Thesis, University of Iowa, Iowa City, IA, 1979.

(12) Kato, M.; Yamabe, M. *J. Chem. Soc., Chem. Commun.* **1981**, 1173.

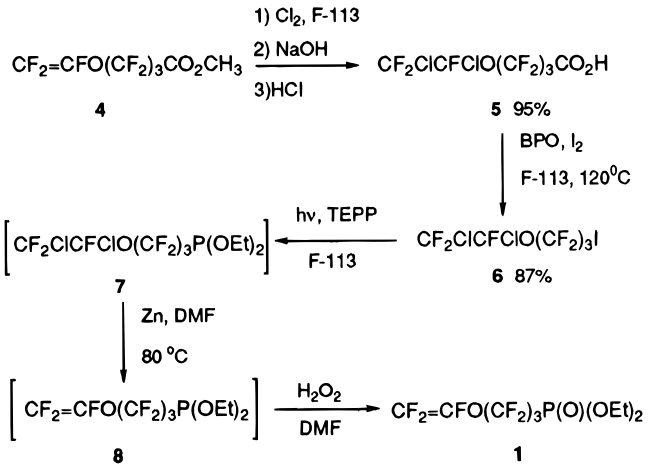
(13) Kato, M.; Akiyama, K.; Akatsuka, Y.; Yamabe, M. *Repr. Res. Lab.; Asahi Glass Co., Ltd.* **1982**, *32*, 117.

(14) Nair, H. K.; Burton, D. J. *Tetrahedron Lett.* **1995**, *36*, 347.

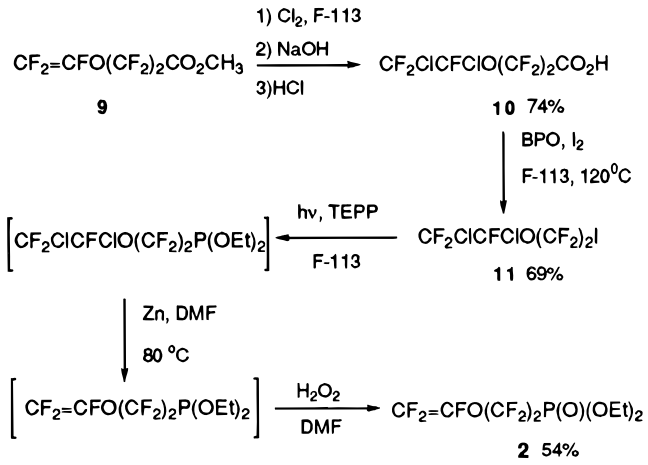
(15) Presented in part at the 12th Winter Fluorine Conference. Pedersen, S. D.; Qiu, Z-M.; Qiu W.; Kotov, S.; Burton, D. J. *Abstracts of Papers*, 12th Winter Fluorine Conference, St. Petersburg, FL; American Chemical Society: Washington, DC, 1995; Abstract P68.

(16) Kotov, S.; Pedersen, S. D.; Qiu, W.; Qiu, Z-M.; Burton, D. J. *J. Fluorine Chem.*, in press.

Scheme 9. Synthesis of Phosphonate Ester 1



Scheme 10. Synthesis of Phosphonate Ester 2



Results and Discussion

I. $(EtO)_2P(O)(CF_2)_3OCF{=}CF_2$ (1). Our initial efforts to produce trifluorovinyl ethers containing phosphonate ester groups were based on the work reported by the Asahi Glass Co.[13] Kato *et al.* produced a trifluorovinyl ether containing a dimethyl phosphonate ester from methyl 4-trifluoroethenoxy-2,2,3,3,4,4-hexafluorobutanoate, **4**. The Kato *et al.* reaction sequence is illustrated in Scheme 7. We attempted to use a similar sequence of reactions to produce phosphonate esters **1** and **2**. However, we found several problem areas in our synthetic efforts that had to be corrected to achieve acceptable yields of phosphonate **1**.

Protection of the trifluorovinyl group with excess chlorine in 1,1,2-trichloro-1,2,2-trifluoroethane (F-113) and saponification of the ester moiety of **4** (Scheme 9) proved quite successful and occurred in nearly quantitative yields (95%). Carboxylic acid **5** could be decarboxylated with benzoyl peroxide in the presence of iodine in F-113 at 120 °C in a sealed tube. The yields of the fluorinated iodide **6** were moderate to good. It proved to be quite difficult to completely dry the hygroscopic fluorinated carboxylic acid **5**. It should be noted that the Hunsdicker reaction[17] was rejected as a possible route to convert the carboxylic acid **5** to the fluorinated iodide, **6**, because the silver salts employed in the Hunsdicker reaction must be completely dry.

The carbon−iodine bond in **6** was replaced with a carbon−phosphorus linkage *via* a photoreaction with tetraethyl pyrophosphite (TEPP). As described by Nair and Burton,[14] the fluorinated iodide **6** was placed in a quartz Rotoflo tube with TEPP and a small amount of F-113 and irradiated at 254 nm for 18 h. The resulting phosphonite **7** was not isolated. Occasionally, if the reaction was irradiated after the total consumption of the fluorinated iodide **6**, the overall yield of final phosphonate **1** was severely reduced. In order to maximize the yield of **1**, the consumption of fluorinated iodide **6** had to be closely monitored by ^{19}F NMR and the irradiation stopped shortly after it was completely consumed.

Kato *et al.*[13] oxidized the protected phosphonite **7** directly. Attempts to oxidize the phosphonite **7** followed by dechlorination, however, always resulted in significant amounts of mono- and bis-dealkylated products. Kato *et al.*[13] noted that they were troubled also by the dealkylation of the phosphonate when deprotecting the trifluorovinyl ether moiety. They corrected the problem by reacting the mixture of phosphonate, monophosphonic acid, and phosphonic acid with phosphorus pentachloride to produce a mixture of phosphoryl chlorides. The phosphoryl chloride was then converted to the methyl phosphonate by stirring with methanol (Scheme 7).

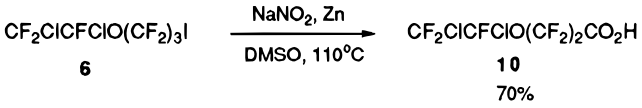
Initial attempts to relieve the problem of the dealkylation of the protected phosphonate as Kato *et al.* described proved to be highly unsuccessful in our hands. The major complication in the sequence proved to be isolation of the phosphoryl chlorides. Kato *et al.*[13] distilled the phosphoryl chlorides directly from the reaction mixture as they were formed. However, attempts to repeat this process produced only very poor yields of the desired chlorides. The reaction mixture always produced a solid, tarlike substance that yielded only small amounts of the phosphoryl chlorides.

This problem was overcome when it was discovered that deprotection of the trifluorovinyl ether moiety prior to oxidation results in no dealkylation of the phosphonite **7**. In our improved synthetic pathway (Scheme 9), the intermediate phosphonite **7** is deprotected with activated zinc in *N*,*N*-dimethylformamide (DMF) at 80 °C for 4 h. The dechlorinated phosphonite **8** is then oxidized. Kato *et al.*[13] utilized *tert*-butyl hydroperoxide at −5 °C. We found that 30% hydrogen peroxide (aqueous) could be successfully employed as an oxidant in DMF solvent at 0 °C. The fact that dealkylation is prevented when the phosphonite **7** is deprotected first and oxidized second allows the synthesis in good yields (69% based on starting iodide **6**) of the perfluorinated diethyl phosphonate **1** without isolation of the troublesome phosphoryl chlorides. This reaction sequence (Scheme 9) also provides the phosphonate ester from the fluorinated iodide **6** without isolation of either the protected phosphonite or the deprotected phosphonite. Effectively, the production of the diethyl phosphonate **1** from the fluorinated iodide **6** is a one-pot synthesis, increasing both the simplicity and yield of the diethyl 1,1,2,2,3,3,5,6,6-nonafluoro-4-oxa-5-hexenylphosphonate, **1**.

II. $(EtO)_2P(O)(CF_2)_2OCF{=}CF_2$ (2). Similarly, diethyl 1,1,2,2,4,5,5-heptafluoro-3-oxa-4-pentenylphosphonate, **2**, could be prepared from methyl 3-trifluoroethenoxy-2,2,3,3-tetrafluoropropanoate, **9**. Scheme 10 demonstrates the reaction sequence. The protection and saponification of **9** again occurred in an almost quantitative yield (74%) to produce the protected carboxylic acid **10**. The fluorinated iodide **11** was synthesized by decarboxylation of

(17) Hudlicky, M. *Chemistry of Organic Fluorine Compounds*; John Wiley and Sons Inc.: New York, 1976; p 225.

Scheme 11. An Alternative Synthesis of Short-Chain Carboxylic Acid 10

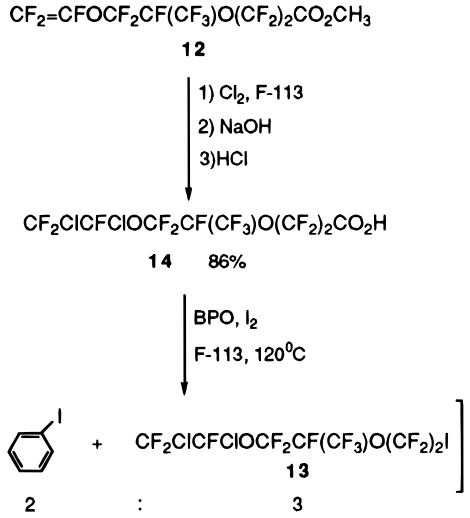


10 using benzoyl peroxide and iodine in F-113 at 120 °C. However, a significantly lower yield (69%) of the iodide, **11**, was obtained than with the longer chain analogue. The lower boiling point of the short-chain iodide may contribute to some of the loss in the yield due to difficulties in the separation of it from the reaction byproducts. Subsequent photochemical reaction of iodide **11** with TEPP in a quartz Rotoflo tube for 20 h afforded the crude protected phosphonite. The crude protected phosphonite was dechlorinated using zinc dust in DMF and then oxidized at 0 °C using hydrogen peroxide yielding the desired diethyl 1,1,2,2,4,5,5-heptafluoro-3-oxa-4-pentenylphosphonate, **2**. The overall yield of phosphonate **2** was 54% based on fluorinated iodide **11**.

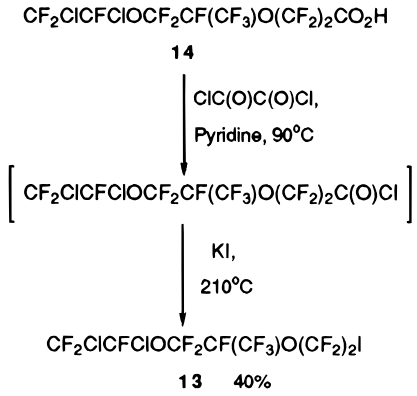
Initially, we lacked access to methyl 3-trifluoro-2,2,3,3-tetrafluoropropanoate, **9**; however, we did have access to methyl 4-trifluoroethenoxy-2,2,3,3,4,4-hexafluorobutanoate, **4**. We synthesized the short-chain, protected carboxylic acid **10** from the iodide **6** that was discussed above. It is known that the iododifluoromethyl terminus of perfluoroalkyl iodides can be oxidized to the corresponding carboxylic acid by sodium nitrite and zinc in dimethyl sulfoxide (DMSO).[18] Since we had already synthesized 1,2-dichloro-6-iodo-1,1,2,4,4,5,5,6,6-nonafluoro-3-oxahexane, **6**, we oxidized **6** using sodium nitrite and zinc in DMSO at 110 °C. This reaction yielded 70% of the desired, protected carboxylic acid **10**, Scheme 11. This carboxylic acid in turn could be employed in the sequence depicted in Scheme 10 to produce the useful iodide intermediate **11**. In effect, the carbon chain of methyl 4-trifluoroethenoxy-2,2,3,3,4,4-hexafluorobutanoate, **4**, was shortened by two carbons using two consecutive iododecarboxylation reactions. The synthesis of diethyl 1,1,2,2,4,5,5-heptafluoro-3-oxa-4-pentenylphosphonate, **2**, could be carried out directly from methyl 3-trifluoroethenoxy-2,2,3,3-tetrafluoropropanoate, **9**, Scheme 10, or indirectly by employing the oxidation of 1,2-dichloro-6-iodo-1,1,2,4,4,5,5,6,6-nonafluoro-3-oxahexane, **6**, to synthesize carboxylic acid **10**.

III. $(EtO)_2P(O)(CF_2)_2OCF(CF_3)CF_2OCF{=}CF_2$ (3). Attempts to produce the longer, branched chain phosphonate ester, **3**, using the reaction sequences described above (Schemes 9 and 10) with methyl 6-trifluoroethenoxy-5-trifluoromethyl-4-oxa-2,2,3,3,5,6,6-heptafluorohexanoate, **12**, were complicated due to an isolation problem. Scheme 12 demonstrates the reactions employed to produce the desired intermediate iodide, **13**, from carboxylate ester **12**. Protection of the trifluorovinyl ether functionality with excess chlorine and saponification of the corresponding ester produced the chlorinated acid, **14**, in an excellent yield (86%). The protected carboxylic acid, **14**, could then be decarboxylated to produce the corresponding iodide, **13**. The decarboxylation produces a significant amount of iodobenzene from the decarboxylation of benzoic acid, which arises from the thermal decomposition of benzoyl peroxide. When the shorter, linear chained iodides were synthesized, the byproduct, iodobenzene, could be efficiently separated by

Scheme 12. Attempted Synthesis of Branched-Chain Iodide 13, Resulting in a Low Boiling Azeotrope of 13 and Iodobenzene



Scheme 13. Synthesis of Branched-Chain Iodide 13



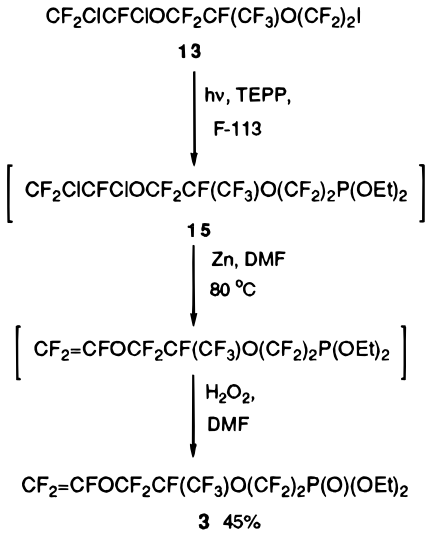
distillation from the desired fluorinated iodide. However, the iodide, **13**, could not be separated from iodobenzene. When the organic material from the reaction was distilled at 90−92 °C at 60 mmHg, a 3:2 mixture of **13** and iodobenzene distilled out. Sequential fractional distillations of this mixture using a 6 cm Vigreux column and an 8 in. spinning band column failed to change the ratio of iodobenzene to the desired iodide **13**. It is surmised that these two materials produce a low boiling azeotrope. Attempts to rectify this problem using *tert*-butyl peroxide in place of benzoyl peroxide proved unsuccessful due to the incomplete decarboxylation of the carboxylic acid, **14**. It was concluded that a more efficient method was required to produce the fluorinated iodide, **13**.

In 1958, Krespan[19] reported that perfluorinated acid chlorides would thermally decarbonylate in the presence of potassium iodide to yield the corresponding perfluorinated alkyl iodides. Conversion of carboxylic acid, **14**, to the acid chloride was accomplished using oxalyl chloride and pyridine at 90 °C for 4 h, Scheme 13. The acid chloride was distilled from the reaction mixture, and placed in a Hastalloy-C pressure reactor with finely ground potassium iodide. The mixture was heated at 210 °C until a constant pressure of 350−400 psi was maintained in the pressure reactor (3−4 h). Workup and distillation yielded 40% of the desired 1,2-dichloro-

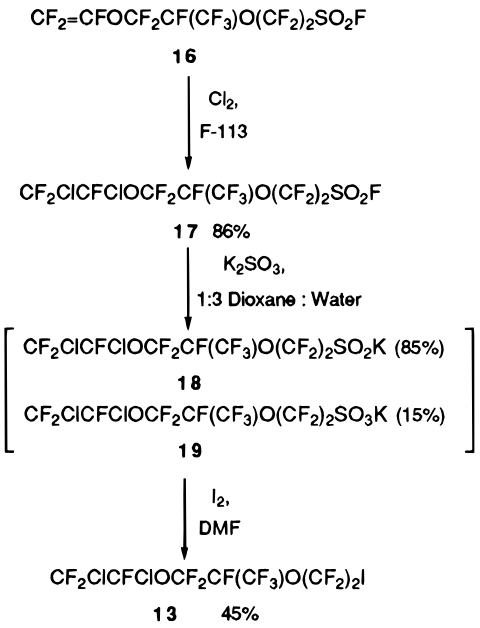
(18) Chen, Q-Y.; Qiu, Z-M. *Acta Chim. Sin.* **1988**, *46*, 39.

(19) Krespan, C. G. *J. Chem. Soc.* **1958**, *23*, 2016.

Scheme 14. Synthesis of Branched-Chain Phosphonate Ester 3



Scheme 15. Synthesis of Branched-Chain Iodide 13 from the Sulfonyl Fluoride 16



1,1,2,4,4,5,7,7,8,8-decafluoro-5-trifluoromethyl-8-iodo-3,6-dioxaoctane, **13**.

Once the iodide, **13**, had been cleanly synthesized and isolated, it was photolyzed with TEPP to produce the branched phosphonite **15**, as shown in Scheme 14. Phosphonite **15** could be dechlorinated with zinc in DMF, and oxidized by hydrogen peroxide to yield 45% of diethyl 1,1,2,2,4,5,5,7,8,8-decafluoro-4-trifluoromethyl-3,6-dioxa-7-octenylphosphonate, **3**. Except for the change in the synthesis of the branched iodide, **13**, all three of the phosphonate esters **1**, **2**, and **3** can be synthesized from their corresponding starting methyl carboxylate esters (**4**, **9**, **12**) *via* the corresponding iodides (**6**, **11**, **13**).

The somewhat disappointing yield of **13** and the availability of 5-trifluoroethenoxy-4-trifluoromethyl-3-oxa-1,1,2,2,4,5,5-heptafluoropentylsulfonyl fluoride, **16** (Scheme 15), prompted us to examine an alternative synthetic route to the branched iodide **13**. Hu and co-workers[20] have closely examined the conversion of fluorinated alkylsulfonyl fluorides to fluorinated alkylsulfinate salts *via* reduction by sodium sulfite (K_2SO_3), followed by iododesulfination of the alkylsulfinates to produce alkyl iodides. These reactions have been used to synthesize several fluorinated alkyl iodides.[20] We investigated the application of this synthetic methodology to **16**.

First, the sulfonyl fluoride was protected using excess chlorine to produce the protected sulfonyl fluoride **17** in a nearly quantitative yield. Following the methodology of Hu and co-workers, the sulfonyl fluoride was reduced to the potassium sulfinate salt, **18**. The potassium sulfonate **19** was found to be the major byproduct of this reaction (Scheme 15). The amount of this sulfonate byproduct must be minimized, since the sulfonate salt does not undergo iododesulfination to form the corresponding fluorinated alkyl iodide. Hu and co-workers report that the most efficient solvent system for the reduction reaction to synthesize potassium fluorosulfinate salts is a mixture of dioxane and water. We found that a 1:1 mixture of dioxane and water produced a 1:1 mixture of desired sulfinate **18** and undesired sulfonate **19**. However, as the ratio of dioxane and water was varied, the ratio of sulfinate salt to sulfonate salt was improved. We found that production of the sulfinate salt was maximized (85%) and production of sulfonate salt was minimized (15%) when a 1:3 mixture of dioxane and water was utilized as the solvent system for the reduction of **17** to **18**. The ratio of sulfinate salt **18** to sulfonate salt **19** was easily determined by integration of the ^{19}F NMR signals of $C\mathbf{F}_2SO_2K$ (−133.6 ppm) versus $C\mathbf{F}_2SO_3K$ (−117.5 ppm).

After the salt mixture was recrystallized and dried, the mixture was treated with iodine in DMF solvent to produce the fluorinated iodide **13** in 45% yield based on protected sulfonyl fluoride **17**. Again, once the fluorinated iodide, **13**, was synthesized from the sulfonyl fluoride, the iodide could be used as the starting material for the photoreaction with TEPP as shown in Scheme 14. The yield of iodide **13** was somewhat disappointing from the starting sulfonyl fluoride; however, these reactions were amenable to scale-up and allowed a large amount of the desired branched iodide, **13**, to be produced in much shorter time than the corresponding synthesis that utilized **12** as the starting material.

Conclusion

Three novel fluorinated vinyl ethers were synthesized for polymerization with tetrafluoroethylene. The vinyl ethers all contained diethyl phosphonate ester groups. These monomers allow the introduction of phosphonic acid groups into perfluoropolymeric membranes. The novel phosphonate esters mimic the commercially available monomers that are based on the sulfonyl fluoride and carboxylic acid functionalities. It was shown that the phosphonate ester moiety could be incorporated using a series of reactions starting from the corresponding iodides. The iodides were converted to the corresponding phosphonites using a photoreaction with tetraethyl pyrophosphite, followed by oxidation with hydrogen peroxide to prepare the desired diethyl phosphonate esters. It was demonstrated that the intermediate iodides could be synthesized either by decarboxylation of the carboxylic acid functionalities or from the corresponding iododes-

(20) (a) Hu, C-M.; Huang, W-Y.; Huang, B-N. *J. Fluorine Chem.* **1983**, *23*, 193. (b) Hu, C-M.; Huang, W-Y.; Huang, B-N. *J. Fluorine Chem.* **1983**, *23*, 229.

ulfination of a sulfonyl fluoride starting material. This synthetic strategy produced moderate to good overall yields of the desired fluorinated vinyl ethers containing phosphonate ester groups.

Experimental Section

General. All of the boiling points are uncorrected. The ^{19}F, ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded in $CDCl_3$ solvent. All of the chemical shifts are reported in parts per million downfield (positive) of the standard: TMS for ^{1}H and ^{13}C, external 85% H_3PO_4 for ^{31}P, and $CFCl_3$ for ^{19}F NMR. FT-IR spectra were recorded as CCl_4 solutions and are reported in wavenumbers (cm^{-1}). Gas chromatography/mass spectroscopy (GC-MS) spectra were obtained at 70 eV in the electron-impact mode. GLPC analyses were performed on a 5% OV-101 column with a thermal conductivity detector. High-resolution mass spectral determinations were made at the University of Iowa High Resolution Mass Spectrometry Facility. A 1-ft, silvered, vacuum-jacketed spinning band appparatus with a Teflon band was employed for the final purification of the phosphonates. All of the reactions were carried out under an atmosphere of nitrogen in oven-dried glassware with magnetic stirring, unless noted otherwise. Photochemical reactions were carried out in a quartz Rotoflo tube in a photoreactor equipped with 254 nm bulbs. DMF was distilled at a reduced pressure from CaH_2. Zinc (325 mesh, Aldrich) was activated by washing with dilute HCl and then dried *in vacuo* at room temperature. All of the reagents were obtained from common commercial sources except $CF_2{=}CFO(CF_2)_3CO_2CH_3$, **4** (Asahi Glass Co.), $CF_2{=}CFO(CF_2)_2CO_2CH_3$, **9** (Dow Chemical Co.), $CF_2{=}CFOCF_2CF(CF_3)O(CF_2)_2SO_2F$, **16** (Shangai Institute of Organic Chemistry), and $CF_2{=}CFOCF_2CF(CF_3)O(CF_2)_2CO_2CH_3$, **12** (E. I. du Pont de Nemours and Co.).

Preparation of 6,7-Dichloro-5-oxa-2,2,3,3,4,4,6,7,7-nonafluoroheptanoic Acid (5). A three-necked, round-bottomed flask equipped with a dry ice condenser, a N_2(g) inlet, a magnetic stir bar, and an isopropyl alcohol bath was charged with 150 g (490 mmol) of $CF_2{=}CFO(CF_2)_3CO_2CH_3$, **4**, and 100 mL of F-113 ($CF_2ClCFCl_2$). The isopropyl alcohol bath was cooled to −10 °C, and gaseous chlorine was condensed into the reaction flask until the solution remained bright yellow. The flask was warmed to room temperature (approximately 3 h), adding additional gaseous chlorine as necessary to maintain the yellow color. When the solution reached room temperature and the yellow color persisted, the dry ice condenser was removed, the reaction flask was fitted with a flash distillation head, and the F-113 was removed *in vacuo*. The residue remaining after the flash distillation was dissolved in 175 mL of methanol and cooled to −5 °C in an ice/salt water bath, then 22 g (550 mmol) of NaOH was added with vigorous stirring. The solution was warmed to room temperature and then stirred for 16 h, and the methanol was removed under vacuum. Total removal of the methanol was achieved after 2 days, generally, leaving a solid residue which was dissolved in 150 mL of water and acidified with 100 mL of concd HCl. The reaction mixture was stirred for 1 h, and the organic layer was isolated. The aqueous layer was washed with diethyl ether (3 × 200 mL). The organic layers were combined, dried over Na_2SO_4, and concentrated to give a residue which was distilled to afford 169 g (95%) of $CF_2ClCFClO(CF_2)_3CO_2H$, **5**, ^{1}H NMR purity 92%, bp 99 °C at 50 mmHg. ^{19}F NMR ($CFCl_3$, $CDCl_3$) −71 (s, 2F), −77 (s,1F), −84 (m, 2F), −119 (s, 2F), −127 (s, 2F) ppm. ^{1}H NMR (TMS, $CDCl_3$) 10.8 (1H) ppm. ^{13}C NMR (TMS, $CDCl_3$) 109 (ttm, J = 270, 35 Hz), 108 (tt, J = 287, 32 Hz), 116 (dt, J = 300, 37 Hz), 117 (tt, J = 290, 32 Hz), 123 (td, J = 300, 35 Hz), 163 (t, J = 30 Hz) ppm. FT-IR (CCl_4) 3078 (m), 1770 (s), 1150 (vs) cm^{-1}.

Synthesis of 1,2-Dichloro-6-iodo-1,1,2,4,4,5,5,6,6-nonafluoro-3-oxahexane (6). A 300 mL Rotoflo tube was charged with 30 g (83 mmol) of $CF_2ClCFClO(CF_2)_3CO_2H$, **5**, 21 g (83 mmol) of benzoyl peroxide, 20 g (83 mmol) of I_2, and 15 mL of F-113. The mixture was degassed and heated at 120 °C for 4 h. The mixture was dissolved in 300 mL of diethyl ether and washed with $NaHSO_3$ (3 × 200 mL), $NaHCO_3$ (3 × 200 mL), and water (3 × 200 mL). The organic layer was dried over Na_2SO_4, and the ether was removed by ambient pressure distillation. The residue was further distilled to yield 63.96 g (87%) of $CF_2ClCFClO(CF_2)_3I$, **6**, bp 96 °C at 118 mmHg. GLPC 95%. ^{19}F NMR ($CFCl_3$, $CDCl_3$) −59 (m, 2F), −71 (m, 2F), −77 (m, 1F), −82 (AB q, 2F), −117 (s, 2F) ppm. ^{13}C NMR (TMS, $CDCl_3$) 92 (tt, J = 320, 41 Hz), 107 (ttt, J = 266, 32, 32 Hz), 115 (tt, J = 291, 34 Hz), 116 (dt, J = 300, 37 Hz), 122 (td, J = 300, 35 Hz) ppm. GCMS (*m/e*, rel.int.) 444, 446, 448 (M^+, 0.69, 0.43, 0.06), 317, 319, 321 ($M^+ - I$, 1.19, 0.76, 0.11), 227 ($M^+ - CF_2ClCFClO$, 58.77), 177 (CF_2I^+, 49.31), 151, 153, 155 ($CF_2ClCFClO^+$, 100, 57.8, 9.12), 127 (I^+, 23.85). HRMS (ZAB-HF) calcd for $C_5F_9OICl_2$ 443.8227, obsd 443.8232. FT-IR (CCl_4) 2361 (w), 1318 (m), 1252 (w), 1200 (s), 1184 (s), 1134 (s), 1016 (m) cm^{-1}.

Synthesis of Diethyl 1,1,2,2,3,3,5,6,6-Nonafluoro-4-oxa-5-hexenylphosphonate (1). A 150 mL quartz Rotoflo tube was charged with 40.7 g (73.3 mmol) of $CF_2ClCFClO(CF_2)_3I$, **6**, 25 g (100 mmol) of $(EtO)_2POP(OEt)_2$, and 25 mL of F-113. The reaction mixture was irradiated in a Rayonet photochemical reactor at 254 nm for 20 h. After vacuum removal of F-113, the residue was dissolved in dry DMF (75 mL) and treated with zinc dust (9.8 g, 150 mmol) at 90 °C for 4 h. The residue was then transferred to a three-necked, round-bottomed flask and treated with 14 mL (150 mmol) of 30% H_2O_2 at −5 °C. On warming to room temperature, the mixture was diluted with 150 mL of Et_2O and washed with NH_4Cl(aq) (3 × 200 mL), $NaHCO_3$(aq) (3 × 200 mL), and H_2O (3 × 200 mL), and the organic layer was dried over Na_2SO_4. After concentration, the residue was purified by silica gel column chromatography (methylene chloride eluent) to afford 19.58 g (51 mmol, 69%) of $(EtO)_2P(O)(CF_2)_3OCF{=}CF_2$, **1**. The monomer was further purified by spinning band distillation. GLPC 99.96%. bp 51 °C at 0.1 mmHg. ^{19}F NMR ($CFCl_3$, $CDCl_3$) −85 (s, 2F), −115 (m, 1F), −122 (m, 1F), −124 (s, 2F) ppm. ^{1}H NMR (TMS, $CDCl_3$) 1.41 (t, J = 7 Hz, 6H), 4.3 (q, J = 7 Hz, 6H) ppm. ^{13}C NMR (TMS, $CDCl_3$) 16 (d, J = 5 Hz), 66 (d, J = 7 Hz), 112 (tt, J = 275, 37 Hz), 115 (tt, J = 275, 37 Hz), 117 (ttm, J = 289, 33 Hz), 130 (ddd, J = 268, 48, 48 Hz), 148 (ddd, J = 278, 278, 54 Hz) ppm. ^{31}P NMR (H_3PO_4, $CDCl_3$) −0.02 (t, J = 89 Hz) ppm. GCMS (*m/e*, relative intensity) 356 ($M^+ - CH_2CH_2$, 0.33), 328 ($M^+ - 2CH_2CH_2$, 1.07), 231 ($M^+ - 153$, 30.5), 109 ($M^+ - 275$, 100), 81 (74.02). HRMS (ZAB-HF) calcd for $C_7H_6F_9O_4P$ 355.9860, obsd 355.9862. FT-IR (CCl_4) 1335 (m), 1288 (m), 1166 (s), 1024 (s) cm^{-1}.

Preparation of 5,6-Dichloro-4-oxa-2,2,3,3,5,6,6-heptafluorohexanoic Acid (10) *via* Methyl 4-Oxa-2,2,3,3,5,6,6-heptafluoro-5-hexenoate (9). A three-necked, round-bottomed flask equipped with a dry ice condenser, a N_2(g) inlet, a magnetic stir bar and an isopropyl alcohol bath was charged with 123 g (480 mmol) of $CF_2{=}CFO(CF_2)_2CO_2CH_3$, **9**, and 100 mL of F-113. The isopropyl alcohol bath was cooled to −10 °C, gaseous chlorine was then condensed into the reaction flask until the solution remained bright yellow. The flask was warmed to room temperature (approximately 3 h), adding additional gaseous chlorine as necessary to maintain the yellow color. When the solution reached room temperature and the yellow color persisted, the dry ice condenser was removed, the reaction flask was fitted with a flash distillation head, and the F-113 was removed *in vacuo*. The residue that was remaining after the flash distillation was dissolved in 200 mL of methanol and 20 mL of H_2O and cooled to −5 °C in an ice/salt water bath, then 24 g (600 mmol) of NaOH was added with vigorous stirring. The solution was warmed to room temperature and stirred for 16 h, and the methanol was removed under vacuum. Total removal of the methanol was achieved after 2 days, generally, leaving a solid residue which was dissolved in 150 mL of water and acidified with 80 mL of concd HCl. The reaction mixture was stirred for 1 h, and the organic layer was isolated. The aqueous layer was washed with CH_2Cl_2 (3 × 200 mL). The organic layers were combined, dried over $MgSO_4$, and concentrated to give a residue which was distilled to afford 110.5 g (74%) of $CF_2ClCFClO(CF_2)_2CO_2H$, **10**, bp 75 °C at 15 mmHg. GLPC 93%. ^{19}F NMR ($CFCl_3$, $CDCl_3$) −71 (d, J = 169 Hz, 1F), −72 (dd, J = 170 Hz, 1F), −77 (m, 1F), −85 (d, J = 142 Hz, 1F), −87 (d, J = 142

Hz, 1F), −122 (s, 2F) ppm. ^{1}H NMR (TMS, $CDCl_3$) 10 (1H) ppm. ^{13}C NMR (TMS, $CDCl_3$) 115 (dt, J = 299, 38 Hz), 116 (tt, J = 290, 33 Hz), 116 (tt, J = 290, 34 Hz), 122 (td, J = 300, 35 Hz), 161 (m) ppm.

Preparation of 5,6-Dichloro-4-oxa-2,2,3,3,5,6,6-heptafluorohexanoic Acid (10) *via* 1,2-Dichloro-6-iodo-1,1,2,4,4,5,5,6,6-nonafluoro-3-oxahexane (6). A 250 mL three-necked, round-bottomed flask fitted with an oil bath, a magnetic stir bar, a water condenser, an internal thermometer, and a nitrogen source was charged with 21.5 g (41 mmol) of $CF_2ClCFClO(CF_2)_3I$, **6**, 12.5 g (180 mmol) of sodium nitrite, and 7.5 g (115 mmol) of zinc in 50 mL of dimethyl sulfoxide. The reaction mixture was stirred at 110 °C for 10 h. After the mixture was cooled, ^{19}F NMR analysis showed a nearly quantitative yield of $CF_2ClCFClO(CF_2)_2CO_2H$, **10**. The reaction mixture was then filtered through a medium frit glass funnel to remove excess zinc. The solution was then acidified with 60 mL (240 mmol) of 4 N HCl. The acidified mixture was then extracted with diethyl ether (4 × 100 mL). The combined organic layers were washed with water (3 × 75 mL) and dried over $MgSO_4$. Filtration and removal of the solvent resulted in 14.05 g of crude $CF_2ClCFClO(CF_2)_2CO_2H$, **10**, which was then distilled at reduced pressure to yield 8.5 g (68%) of $CF_2ClCFClO(CF_2)_2CO_2H$, **10**. bp 53 °C at 1.5 mmHg. GLPC 96%. All of the spectroscopy data were identical to that noted above.

Synthesis of 1,2-Dichloro-5-iodo-1,1,2,4,4,5,5-heptafluoro-3-oxapentane (11). A 300 mL Rotoflo tube was charged with 25 g (80 mmol) of $CF_2ClCFClO(CF_2)_2CO_2H$, **10**, 21 g (83 mmol) of benzoyl peroxide, 20 g (83 mmol) of I_2, and 50 mL of F-113. The mixture was degassed and heated at 120 °C for 4 h. The mixture was dissolved in 500 mL of CH_2Cl_2 and washed with $NaHSO_3$ (3 × 200 mL), $NaHCO_3$ (3 × 200 mL), and water (3 × 200 mL). The organic layer was dried over $MgSO_4$, and the CH_2Cl_2 was removed by ambient pressure distillation. The residue was further distilled to yield 27.2 g (63%) of $CF_2ClCFClO(CF_2)_2I$, **11**, bp = 115−118 °C. GLPC 95%. ^{19}F NMR ($CFCl_3$, $CDCl_3$) −65 (m, 2F), −71 (d, J = 170 Hz, 1F), −71 (dd, J = 170, 7 Hz, 1F), −77 (m, 1F), −86 (ddm, J = 141, 27 Hz, 1F), −88 (dd, J = 143, 6 Hz, 1F) ppm. ^{13}C NMR (TMS, $CDCl_3$) 89 (tt, J = 320, 41Hz), 115 (tt, J = 288, 31 Hz), 115 (dt, J = 300, 37 Hz), 122 (dt, J = 300, 35 Hz) ppm. GCMS (*m*/*e*, relative intensity) 394, 396, 398 (M^+, 1.91, 1.18, 0.16), 309, 311 ($M^+ - ClCF_2$, 0.59, 0.17), 267, 269, 271 ($M^+ - I$, 2.26, 1.41, 0.23), 243 (2.01), 227 ($ICF_2CF_2^+$, 100), 177 (42.11), 151, 153, 155 (22.81, 14.47, 2.44), 135, 137 (58.77, 19.08), 127 (I^+, 17.98). HRMS (ZAB-HF) calcd for $C_4F_7OICl_2$ 393.8259, obsd 393.8252. FT-IR (CCl_4) 1252(m), 1182(vs), 1155(s), 1127(s), 1061(m) cm^{-1}.

Preparation of Diethyl 1,1,2,2,4,5,5-Heptafluoro-3-oxa-4-pentenylphosphonate (2). A 150 mL quartz Rotoflo tube was charged with 6.0 g (15.7 mmol) of $CF_2ClCFClO(CF_2)_2I$, **11**, 7.75 g (30 mmol) of $(EtO)_2POP(OEt)_2$, and 25 mL of F-113. The reaction mixture was irradiated at 254 nm for 20 h in a photochemical reactor. After vacuum removal of F-113, the residue was dissolved in dry DMF (20 mL) and treated with zinc dust (2.0 g, 30 mmol) at 90 °C for 4 h. The residue was then transferred to a three-necked, round-bottomed flask and treated with 4 mL (30 mmol) of 30% H_2O_2 at −5 °C. On warming to room temperature, the mixture was diluted with 100 mL of Et_2O and washed with NH_4Cl(aq) (3 × 100 mL), $NaHCO_3$(aq) (3 × 100 mL), and H_2O (3 × 100 mL), and the organic layer was dried over $MgSO_4$. After concentration, the residue was purified by silica gel column chromatography (methylene chloride eluent) to afford 2.8 g (8.5 mmol, 54%) of $(EtO)_2P(O)(CF_2)_2OCF{=}CF_2$, **2**. The monomer was further purified by spinning band distillation, bp 95 °C at 5 mmHg. GLPC 99.92%. ^{19}F NMR ($CFCl_3$, $CDCl_3$) −86 (s, 2F), −115 (dd, J = 85, 65 Hz, 1F), −123 (dd, J = 109, 87 Hz, 1F), −125 (dt, J = 117, 90 Hz, 2F), −135 (dd, J = 112, 66 Hz, 1F) ppm. ^{1}H NMR (TMS, $CDCl_3$) 1.41 (t, J = 7 Hz, 6H), 4.4 (m, 4H) ppm. ^{13}C NMR (TMS, $CDCl_3$) 15 (s), 65 (s), 105 (m), 115 (m), 130 (dt, J = 270, 48 Hz), 147 (td, J = 280, 54 Hz) ppm. ^{31}P NMR (H_3PO_4, $CDCl_3$) 0.89 (t, J = 87 Hz) ppm. GCMS (*m*/*e*) (333 $M^+ - H$), 307, 279, 259, 234, 209, 181, 137, 109, 91, 81 (100), 65, 45. HRMS (ZAB-HF) calcd for $C_8H_{11}F_7O_4P$ 335.0283, obsd 335.0286. FT-IR (CCl_4) 1329(m), 1281(m), 1168(s), 1139(s), 1123(s) cm^{-1}.

Synthesis of 8,9-Dichloro-2,2,3,3,5,6,6,8,9,9-decafluoro-5-trifluoromethyl-4,7-dioxanonanoic Acid (14). A three-necked, round-bottomed flask equipped with a dry ice condenser, a N_2(g) inlet, a magnetic stir bar, a glass tube that reached below the surface of the solution, and an ice/salt bath was charged with 100 g (237 mmol) of $CF_2{=}CFOCF_2CF(CF_3)OCF_2CF_2CO_2CH_3$, **12**, and 100 mL of F-113 ($CF_2ClCFCl_2$). The ice/salt bath was cooled to 0 °C, and gaseous chlorine was bubbled into the reaction flask until the solution remained bright yellow. The flask was warmed to room temperature (approximately 4 h), adding additional gaseous chlorine as necessary to maintain the yellow color. When the solution reached room temperature and the yellow color persisted, ^{19}F NMR analysis of an aliquot showed that no vinyl fluorines remained. The dry ice condenser was removed, the reaction flask was fitted with a flash distillation head, and the F-113 was removed *in vacuo*. The residue that was remaining after the flash distillation was dissolved in 175 mL of methanol and cooled to −5 °C in an ice/salt water bath, then 12 g (300 mmol) of NaOH was added with vigorous stirring. The solution was warmed to room temperature and then stirred for 12 h, and the methanol was removed *in vacuo*. The residue was then dissolved in ethyl acetate and washed with brine (5 × 150 mL) to remove any remaining MeOH. The ethyl acetate was then removed *via* rotary evaporation and *in vacuo*. The remaining solids were then dissolved in water and acidified with concd HCl (60 mL) under vigorous stirring. The solution was then transferred to a separatory funnel, and the organic layer was isolated. The aqueous layer was washed with diethyl ether (3 × 200 mL). The organic layers were combined, dried over Na_2SO_4, and concentrated to give a residue which was distilled to afford 98.2 g (86%) of $CF_2ClCFClOCF_2CF(CF_3)OCF_2CF_2CO_2H$, **14**, bp 120−122 °C at 23 mmHg. GLPC 91%. ^{19}F NMR ($CFCl_3$, $CDCl_3$) −71.3 (m, 2F), −77.3 (m, 1F), −80.3 (m, 3F), −82 through −86 (m, 4F), −122.3 (s, 2F), −145.7 (m, 1F) ppm. ^{1}H NMR (TMS, $CDCl_3$) 10.44 (s, 1H) ppm. ^{13}C NMR (TMS, $CDCl_3$) 103.29 (dsex, J = 269.76, 38.01 Hz), 106.89 (tt, J = 266.5, 36.1 Hz), 116.1 (tt, 259.6, 32.3 Hz), 116.14 (dt, J = 295.81, 34.0 Hz), 116.7 (td, J = 290.2, 31.4 Hz), 118.8 (qd, J = 289.0, 31.9 Hz), 122.5 (td, J = 300.2, 34.5 Hz), 164.7 (t, J = 30.6 Hz) ppm. FT-IR (CCl_4) 1763 (s), 1195 (s), 1020 (m) cm^{-1}.

Synthesis of 1,2-Dichloro-1,1,2,4,4,5,7,7,8,8-decafluoro-5-trifluoromethyl-8-iodo-3,6-dioxaoctane (13) *via* 8,9-Dichloro-2,2,3,3,5,6,6,8,9,9-decafluoro-5-trifluoromethyl-4,7-dioxanonanoic Acid (14). A 300 mL Rotoflo tube was charged with 40.63 g (85 mmol) of $CF_2ClCFClOCF_2CF(CF_3)OCF_2CF_2CO_2H$, **14**, 21 g (85 mmol) of benzoyl peroxide, 22 g (86 mmol) of I_2, and 30 mL of F-113. The mixture was degassed and heated at 120 °C for 4 h. The mixture was dissolved in 300 mL of diethyl ether and washed with $NaHSO_3$ (3 × 200 mL), $NaHCO_3$ (3 × 200 mL), and water (3 × 150 mL). The organic layer was dried over Na_2SO_4 and the ether was removed by simple distillation. The residue was further distilled at reduced pressure to yield 69 g (73%) of a 40:60 mixture of iodobenzene and $CF_2ClCFClOCF_2CF(CF_3)O(CF_2)_2I$, **13**, bp 90 °C at 60 mmHg. GLPC 60%. ^{19}F NMR ($CFCl_3$, $CDCl_3$) −64 (s, 2F), −71 (AB q, 2F), −77 (m, 1F), −80 (m, 2F), −83 (m, 1F), −84 (m, 3F), −146 (m, 1F) ppm. ^{13}C NMR (TMS, $CDCl_3$) 90 (tt, J = 320, 41Hz), 103 (dsex, J = 270, 38 Hz), 116 (ttd, J = 287, 31, 4 Hz), 116 (dt, J = 300, 39 Hz), 117 (td, J = 291, 30 Hz), 118 (qd, J = 288, 32 Hz), 123 (td, J = 300, 35 Hz) ppm. GCMS (*m*/*e*, relative intensity) 560, 562, 564 (M^+, 1.69, 1.12, 0.18), 393 ($M^+ - CF_2ClCFClO$, 25.1), 227 ($CF_2CF_2I^+$, 61.69), 177 (CF_2I^+, 50.98), 151, 153, 155 (CF_2ClCFO^+, 100, 92.55, 22.25), 127 (I^+, 24.9), 100 (87.45), 69 (CF_3^+, 79.61). FT-IR (CCl_4) 1296 (s), 1203 (s), 1187 (s), 913 (s) cm^{-1}.

Synthesis of 7,8-Dichloro-1,1,2,2,4,5,5,7,8,8-decafluoro-4-trifluoromethyl-3,6-dioxasulfonyl Fluoride (17). A three-necked, round-bottomed flask equipped with a Teflon coated magnetic stir bar, a dry ice−isopropyl alcohol bath, a dry ice−isopropyl alcohol condenser, a low-temperature thermometer, a nitrogen gas inlet, and an inlet for Cl_2 was charged with 500 g (414 mmol) of $CF_2{=}CFOCF_2CF(CF_3)OCF_2CF_2SO_2F$, **16**. The solution was cooled to −5 °C *via* the dry ice−isopropyl

alcohol bath, and excess chlorine gas was bubbled into the solution over 5 h. Once chlorine gas started to condense from the dry ice−isopropyl alcohol condenser, the addition of chlorine gas was stopped and the solution allowed to stir for 1 h. ^{19}F NMR analysis showed no vinyl fluorines remained in the mixture. Excess chlorine was then removed by flash distillation at full vacuum to yield 532 g (86%) of $CF_2ClCFClOCF_2CF(CF_3)O(CF_2)_2SO_2F$, **17**. GLPC 97%. ^{19}F NMR ($CFCl_3$, $CDCl_3$) 45.2 (s, 1F), −71.2 (d, J = 21 Hz, 2F), −77.1 (m, 1F), −79.3 (m, 2F), −80.1 (d, J = 8.4 Hz, 3F), −84.5 (m, 2F), −112.0 (s, 2F) ppm. ^{13}C NMR (TMS, $CDCl_3$) 103.7 (dsex, J = 271.6, 39 Hz), 113.7 (tt, J = 302, 38 Hz), 116.0 (tt, J = 291, 30 Hz), 116.6 (dt, 301, 37.5 Hz), 117.3 (td, J = 290, 29 Hz), 118.4 (qd, J = 287, 31 Hz), 122.8 (td, J = 300, 34.5 Hz) ppm. GCMS (*m/e*, relative intensity) 349 (0.99), 263 (1.03), 169 (22.42), 153 (38.18), 151 (62.42), 67 (100). FT-IR (CCl_4) 1463 (m), 1243 (s), 1207 (m) cm^{-1}.

Synthesis of 1,2-Dichloro-1,1,2,4,4,5,5,7,7,8,8-decafluoro-5-trifluoromethyl-8-iodo-3,6-dioxaoctane (13) *via* the Sulfonyl Fluoride (17). A mixture of $CF_2ClCFClOCF_2CF(CF_3)O(CF_2)_2SO_2F$, **17** (40 g, 80 mmol), K_2SO_3 (48 g, 308 mmol), dioxane (60 mL), and water (180 mL) was stirred at 100 °C for 14 h. The remaining solids were removed *via* vacuum filtration. The filtrate was then dried under vacuum (3 days) to form a solid that was extracted with hot isopropanol (2 × 300 mL). Concentration and vacuum drying (3 days) of the isopropyl alcohol solution gave 30.2 g of crude $CF_2ClCFClOCF_2CF(CF_3)O(CF_2)_2SO_2K$, **18** (contaminated with 15% $CF_2ClCFClOCF_2CF(CF_3)O(CF_2)_2SO_3K$, **19**). The crude sulfinate was treated with iodine (20 g, 80 mmol) in DMF (47 mL) at 62 °C for 3 h. The reaction mixture was then dissolved in 250 mL of Et_2O and washed with $NaHSO_3$(aq) (3 × 200 mL), $NaHCO_3$(aq) (3 × 200 mL), and H_2O (3 × 200 mL). The ether layer was dried over Na_2SO_4 and concentrated to give a residue that was distilled at reduced pressure to yield 19 g (45%) of $CF_2ClCFClOCF_2CF(CF_3)O(CF_2)_2I$, **13**, bp 95 °C at 65 mmHg. GLPC 98%. ^{19}F NMR ($CFCl_3$, $CDCl_3$) −64 (s, 2F), −71 (AB q, 2F), −77 (m, 1F), −80 (m, 2F), −83 (m, 1F), −84 (m, 3F), −146 (m, 1F) ppm. ^{13}C NMR (TMS, $CDCl_3$) 90 (tt, J = 320, 41 Hz), 103 (dsex, J = 270, 38 Hz), 116 (ttd, J = 287, 31, 4 Hz), 116 (dt, J = 300, 39 Hz), 117 (td, J = 291, 30 Hz), 118 (qd, J = 288, 32 Hz), 123 (td, J = 300, 35 Hz) ppm. GCMS (*m/e*, relative intensity) 560, 562, 564 (M^+, 1.69, 1.12, 0.18), 393 ($M^+ - CF_2ClCFClO$, 25.1), 227 ($CF_2CF_2I^+$, 61.69), 177 (CF_2I^+, 50.98), 151, 153, 155 (CF_2ClCFO^+, 100, 92.55, 22.25), 127 (I^+, 24.9), 100 (87.45), 69 (CF_3^+, 79.61). HRMS (ZAB-HF) calcd for $C_7F_{13}O_2ICl_2$ 559.8112, obsd 559.8109. FT-IR (CCl_4) 1464 (m), 1296 (s), 1203 (s), 1187 (s), 913 (s) cm^{-1}.

Synthesis of 1,2-Dichloro-1,1,2,4,4,5,5,7,7,8,8-decafluoro-5-trifluoromethyl-8-iodo-3,6-dioxaoctane (13) Utilizing the Acid Chloride of 8,9-Dichloro-2,2,3,3,5,6,6,8,9,9-decafluoro-5-trifluoromethyl-4,7-dioxanonanoic Acid (14). A 500 mL three-necked, round-bottomed flask equipped with a magnetic stir bar, a submersion thermometer, a water condenser, a rubber septum, and a nitrogen inlet was charged with 30 g (67 mmol) of $CF_2ClCFClOCF_2CF(CF_3)OCF_2CF_2CO_2H$, **14**, and 10.5 g (130 mmol) of pyridine. An immediate exothermic reaction occurred. After the mixture was cooled to room temperature, 8.82 g (70 mmol) of oxalyl chloride was slowly added *via* a syringe. The reaction mixture was then heated to 90 °C for 4 h. The water condenser was then replaced with a simple distillation apparatus, and $CF_2ClCFClOCF_2CF(CF_3)OCF_2CF_2COCl$ and some pyridinium salts were crudely distilled under reduced pressure from the reaction mixture, bp 130 °C at 40 mmHg. GLPC 98%. ^{19}F NMR ($CFCl_3$, $CDCl_3$) −71.2 (m, 2F), −77.3 (m, 1F), −80.1 (d, J = 8.4 Hz, 3F), −81.0 through −85.5 (m, 4F), −116.6 (s, 2F), −145.7 (s, 1F) ppm. A solution of 25 g (54 mmol) of $CF_2ClCFClOCF_2CF(CF_3)OCF_2CF_2COCl$ and 9.96 g (60 mmol) of finely ground potassium iodide were then placed in a 250 mL Parr Hastaloy-C pressure reactor equipped with a mechanical stirrer, a temperature probe, a heating mantle, and a pressure gauge. The reaction mixture was then heated to 210 °C. When the pressure had reached a constant pressure (350−400 psi), the reaction mixture was cooled, dissolved in 300 mL of diethyl ether, and washed with $NaHSO_3$(aq) (3 × 200 mL), $NaHCO_3$(aq) (3 × 200 mL), and H_2O (3 × 200 mL). The ether layer was dried over Na_2SO_4 and concentrated to give a residue that was distilled at reduced pressure to yield 12.3 g (40%) of $CF_2ClCFClOCF_2CF(CF_3)O(CF_2)_2I$, **13**, bp 95 °C at 65 mmHg. GLPC 98%. All of the spectroscopy data were identical to that noted above.

Preparation of Diethyl 1,1,2,2,4,5,5,7,8,8-Decafluoro-4-trifluoromethyl-3,6-dioxa-7-octenylphosphonate (3). A mixture of $CF_2ClCFClOCF_2CF(CF_3)O(CF_2)_2I$, **13** (20 g, 35 mmol), $(EtO)_2POP(OEt)_2$ (12 g, 45 mmol), and F-113 (5 mL) was irradiated in a Rayonet photochemical reactor in a quartz tube at 254 nm for 20 h. After the F-113 was removed *in vacuo*, the mixture was dissolved in DMF (60 mL) and treated with zinc dust (3.0 g, 46 mmol) at 90 °C for 4 h. The solution was then transferred to a round-bottomed flask and treated with 14 mL (∼75 mmol) of 30% H_2O_2 at −10−0 °C. After the mixture was warmed to room temperature (2 h), it was diluted with 150 mL of Et_2O and washed with NH_4Cl(aq) (3 × 200 mL), $NaHCO_3$(aq) (3 × 200 mL), and H_2O (3 × 200 mL). The Et_2O fraction was then dried over Na_2SO_4 and concentrated to give a residue that was purified by silica gel column chromatography (methylene chloride eluent) to afford 10 g (45%) of $CF_2{=}CFOCF_2CF(CF_3)O(CF_2)_2P(O)(OEt)_2$, **3**. The monomer was further purified by spinning band distillation, bp 89 °C at 0.2 mmHg. GLPC 99.97%. ^{19}F NMR ($CFCl_3$, $CDCl_3$) −80 (s, 3F), −82 (m, 2F), −85 (s, 2F), −114 (dd, J = 85, 66 Hz, 1F), −122 (dd, J = 124, 85 Hz, 1F), −125 (d, J = 91 Hz, 2F), −136 (ddm, J = 124, 66 Hz, 1F), −145 (t, J = 22 Hz, 1F) ppm. ^{1}H NMR (TMS, $CDCl_3$) 1.4 (t, J = 7 Hz, 6H), 4.3 (q, J = 7 Hz, 4H) ppm. ^{13}C NMR (TMS, $CDCl_3$) 16.3 (d, J = 7 Hz), 66 (d, J = 6.4 Hz), 103 (dsex, J = 268, 35 Hz), 110 (tt, J = 275, 36 Hz), 113 (tt, J = 275, 36 Hz), 117 (tm, J = 283 Hz), 118 (dqt, J = 288, 312, 1 Hz), 130 (ddd, J = 27, 48, 28 Hz), 147 (ddd, J = 280, 280, 53 Hz) ppm. ^{31}P NMR (H_3PO_4, $CDCl_3$) 0 (t, J = 91 Hz) ppm. GCMS (*m/e*, relative intensity) 500 (M^+, 0.02), 347 ($M^+ - CF_2{=}CFO-28$, 6.63), 197 (4.11), 181 (21.43), 137 (66.63), 109 (100). HRMS (ZAB-HF) calcd for $C_{11}H_{11}F_{13}O_5P$ 501.0137, obsd 501.0139. FT-IR (CCl_4) 1335(m), 1287(m), 1188(s), 1025(s), 908(vs) cm^{-1}.

Acknowledgment. We thank the National Science Foundation, ARPA, and the Office of Naval Research (ONR Contract N00014-92-J-1848) for financial support of this work. S. D. Pedersen thanks the ONR for an AASERT Fellowship (N00014-93-1-1070). We also thank Asahi Glass, DuPont, and Dow Chemical for assistance with monomer precursors.

Supporting Information Available: Copies of ^{13}C NMR spectra for compounds **1**, **2**, **3**, **5**, **6**, **10**, **11**, **13**, **14**, and **17** are available (10 pages). This material is contained in libraries on microfiche, immediately follows this article on the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

JO961086A