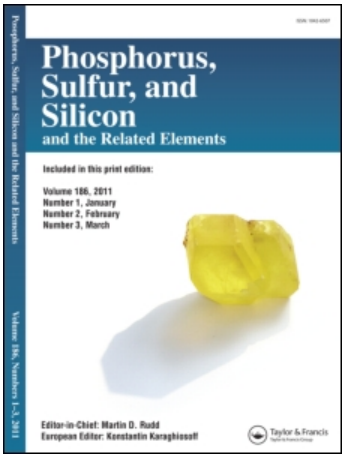

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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D. K. Rohrbaugh[a]; F. R. Longo[b]; H. D. Durst[a]; S. Munavalli[b]
[a] US. Army, Edgewood Chemical Biological Center, APG, MD [b] Geo-Centers, Inc., APG, MD

To cite this Article Rohrbaugh, D. K. , Longo, F. R. , Durst, H. D. and Munavalli, S.(2001) 'Microwave Induced and Photocatalyzed Hydrophosphorylation Reactions of Perfluoroolefins', Phosphorus, Sulfur, and Silicon and the Related Elements, 176: 1, 201 — 214
To link to this Article: DOI: 10.1080/10426500108055119
URL: http://dx.doi.org/10.1080/10426500108055119

Phosphorus, Sulfur and Silicon, 2001, Vol. 176, pp. 201–214

1042-6507/01 $12.00 + .00

MICROWAVE INDUCED AND PHOTOCATALYZED HYDROPHOSPHORYLATION REACTIONS OF PERFLUOROOLEFINS

D. K. Rohrbaugh,[1] *F. R. Longo,*[2] *H. D. Durst,*[1] *and S. Munavalli*[2,*]
[1]*U.S. Army, Edgewood Chemical Biological Center, APG, MD 21010 and* [2]*Geo-Centers, Inc., P.O. Box 68 Gunpowder Branch, APG, MD 21010*

(Received May 8, 2001; In final form May 22, 2001)

Microwave induced and UV-catalyzed hydrophosphorylation reactions of perfluoroolefins with hydrogen dimethylphosphonate have been examined and found to furnish hydrophosphorylated compounds among other products. This communication attempts to rationalize the formation of compounds and their GC-MS characterization.

Keywords: Hydrophosphorylation; microwave-initiation; photocatalysis; perfluoro-olefins

INTRODUCTION

Recently phosphonic acid derivatives have attracted considerable attention, since they are finding increasing application and use as synthetic intermediates, flame retardants, and herbicides, etc. There is also considerable current interest in the synthesis of fluorine containing organophosphorus compounds[1a] and in the preparation of biologically active phosphonic acid derivatives.[1b] Hydrogen mono- and dialkylphosphonates (H-phosphonates) have found particular use in the phosphorylation reactions and in the synthesis of oligonucleotides.[2] Both acids and bases react with H-dialkylphosphonates,[2c] indicating facile removal of the hydrogen directly attached to the phosphorus atom. Among other reactions, they are also known to add to carbon-carbon multiple bond[3a] and to attack carbonyl group.[3b] Although H-phosphonates are resistant to oxidation, they can be transformed into phosphates. It has been reported that air oxidation of trialkylphosphines and trialkylphosphites gives various oxidation products including phosphates via free radical

processes.[4a] The loss of the alkyl moiety during oxidation has also been recorded.[4b–d]

It has been reported that the presence of fluorine and fluorine containing groups in organic molecules considerably enhances their biopharmacological properties.[5] Also, the properties and reactivity of the carbon-carbon multiple bond are said to be considerably altered by the attachment of fluorine atoms to the carbons joined by multiple bond.[6] Although it is difficult to generate radical cations from perfluroolefins, the addition reactions can be catalyzed by Lewis acids.[7] The claim of ionic addition of halogens to perfluoroolefins[8a] has been questioned.[8b] In continuation of our interest in the synthesis of bioactive organofluorine compounds,[9] we have now investigated the reaction of H-dimethylphosphonate with perfluoroolefins and this paper presents the results thus obtained.

RESULTS AND DISCUSSION

There are not many examples of the reaction of perfluoroolefins with phosphorus compounds, for the usual classical routes to dialkylphosphonates cannot be successfully applied to the synthesis of fluorine containing phosphorus compounds.[10] When fluorine is attached either directly to, or is carried by a group linked to phosphorus, it is said to reduce the latter's nucleophilicity.[1a] Early work on the addition of dialkylphosphonates to carbon-carbon double bond has been discussed.[11a] The addition reaction in alcohol yields the C_2-adduct, while the same reaction in the presence of a peroxide gives the C_1-adduct.[11b] The Lewis acid catalyzed additions to perfluoroolefins have been discussed recently.[6] In a series of interesting papers, Chambers and coworkers have described the addition of diazomethane, alcohols and ethers to perfluoroolefins.[12] H-dialkylphosphonate has been reported to add to α-nitrostyrene in the presence triethylamine to give the respective β-phosphonate derivative.[13a] Addition to 1-(3,3-dimethylallenyl) phosphonate yields 1-propenyl-1,2-diphosphonate.[13b] However, a similar reaction has been reported to give a diphosphonate which had lost the allenyl moiety.[13c] Intramolecular dealkylation has been observed in the reaction of triethylphosphite.[13d] Trialkylborates and ethers have also been reacted with perfluoroalkenes.[14]

Figures 1 and 2 respectively summarize microwave induced and photo-catalyzed reactions of 3-(perfluorophenyl)pentafluoropropene and perfluoroisobutylene with H-dimethylphosphonate. Addition of trifluoromethylsulfenyl chloride as well as hydroboration of

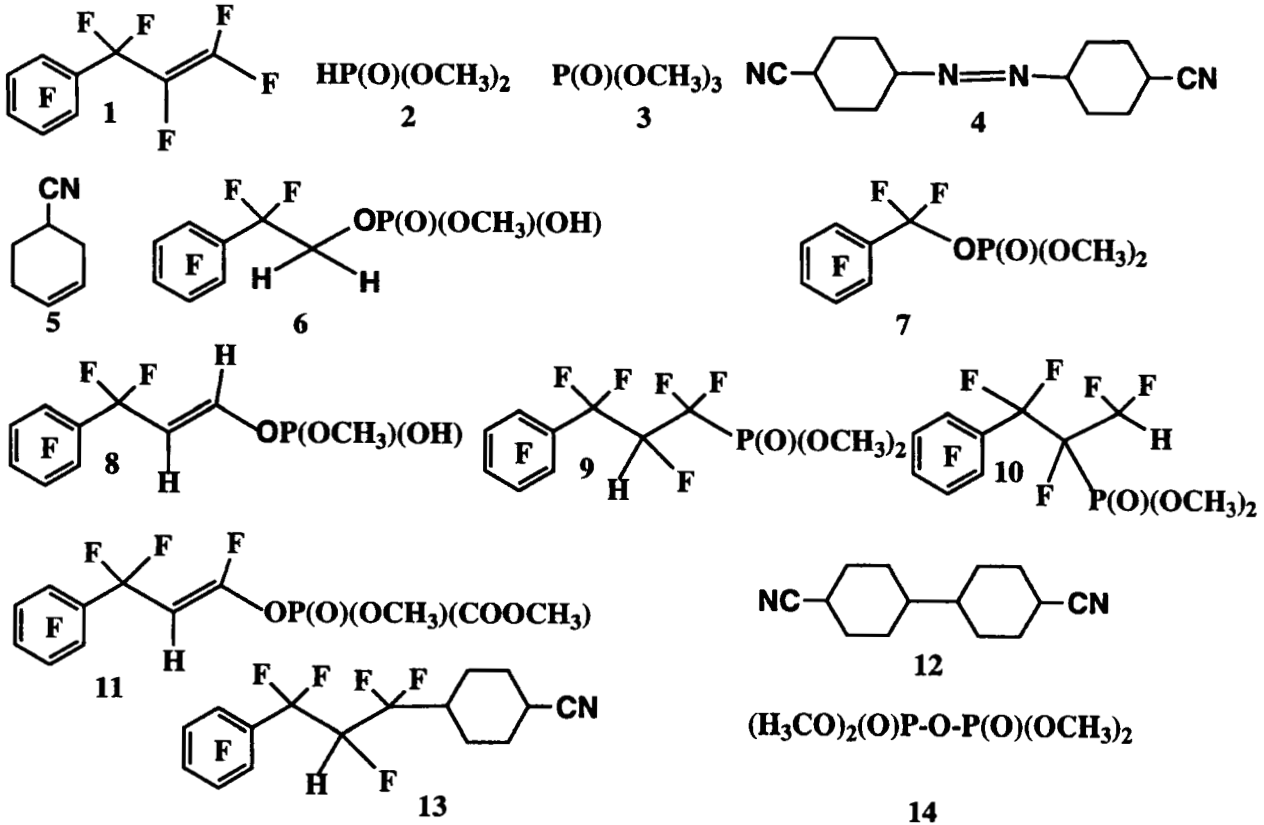

FIGURE 1 Reaction of 3-perfluorophenylpentafluoropropene.

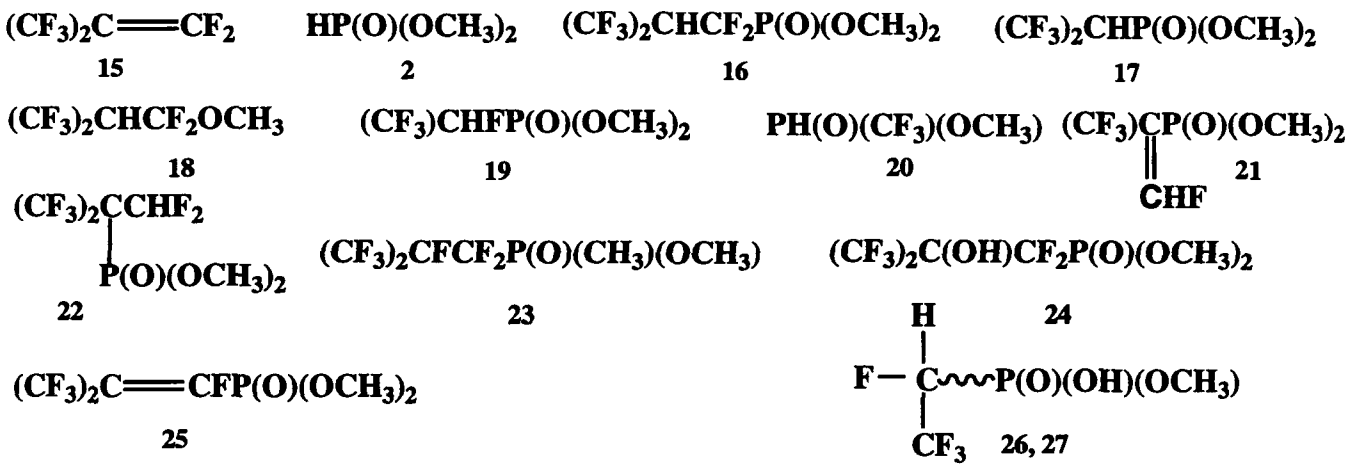

FIGURE 2 Reaction of perfluoroisobutylene.

3-(perfluorophenyl)-pentafluoropropene (**1**, Figure 1) failed to yield the expected product(s). The microwave induced reaction of 3-(perfluorophenyl)-1-pentafluorpropene (**1**, Figure 1) with **H**-dimethylphosphonate (**2**) in the presence of the free radical initiator, 4,4′-azobis(cyclohexanecarbonitrile) (**4**), yielded 14 compounds as indicated by its GC-MS analysis. The probable mechanism of the formation of various compounds thus formed is schematically described in Figure 3. 4-Cyanocyclohexene (**5**) as well as 4,4′-dicyanodicyclohexane (**12**) owe their presence to the free radical initiator (**4**) itself. The formation of methyl[(perfluorobenzyl)methyl] phosphonic acid (**6**) appears to be rather involved. Hydrogen split off from H-dimethylphosphonate (**2**) reacts with 3-(perfluorophenyl) pentafluoropropene (**1**) to give a radical intermediate, which loses a fluorine radical to form perfluorobenzyl-1, 1-difluoroethylene. The latter reacts with phosphonyl radical to yield perfluorobenzylphosphonyl-1, 1-difluoroethyl radical, which in turn splits off difluorocarbene and a CH_2-moiety from the methoxy group to form the phosphonic acid derivative (**6**). The formation of dimethyl(perfluorobenzyl)phosphate (**7**, Figure 1) is straight-forward. This entails the reaction of the perfluorobenzyl radical with phosphoranyl radical. Compound **8**, on the other hand, involves the replacement of $C_{1,2}$-fluorine atoms by hydrogen, addition of the phosphorus moiety and followed by dealkylation. Compounds **9** and **10** are isomers resulting from a simple addition of dimethylphosphonyl radical. Although structure **11** represents a tentative structure, its consideration rests on several observations. Its mass spectrum shows the presence of the perfluorobenzyl ion (m/e = 217). The carbomethoxy group is considered to have been formed from the reaction of the free radical initiator, moisture and phosphonate via the *in situ* formed isocyanate group reacting with methanol to give the carbamate moiety. Indeed, the reaction between phenylisocyanate with the H-phosphonate under similar experimental conditions did form the respective carbamate, confirming the above inference. Compound **12** can be conveniently prepared from the free radical initiator, **4**. Compound **13** results from the cross-coupling reaction of 3-(perfluorophenyl)-1-pentafluoropropenyl radical with 4-cyanocyclohexyl radical, the latter being generated from the free radical initiator itself. The pyrophosphonate **14**, is the oxidation-dehydration product of **2**. The mass spectral fragmentation of the various products is given in the experimental part.

Perfluoroisobutylene (**PFIB**, **15**, Figure 2) is a very highly reactive molecule, which participates in both heterolytic and homolytic reactions. It reacts with electrophiles as well as with nucleophiles. Its interesting chemistry has been the subject of an exhaustive review.[15] Free radical addition of Br_2 to PFIB has been described.[16a]

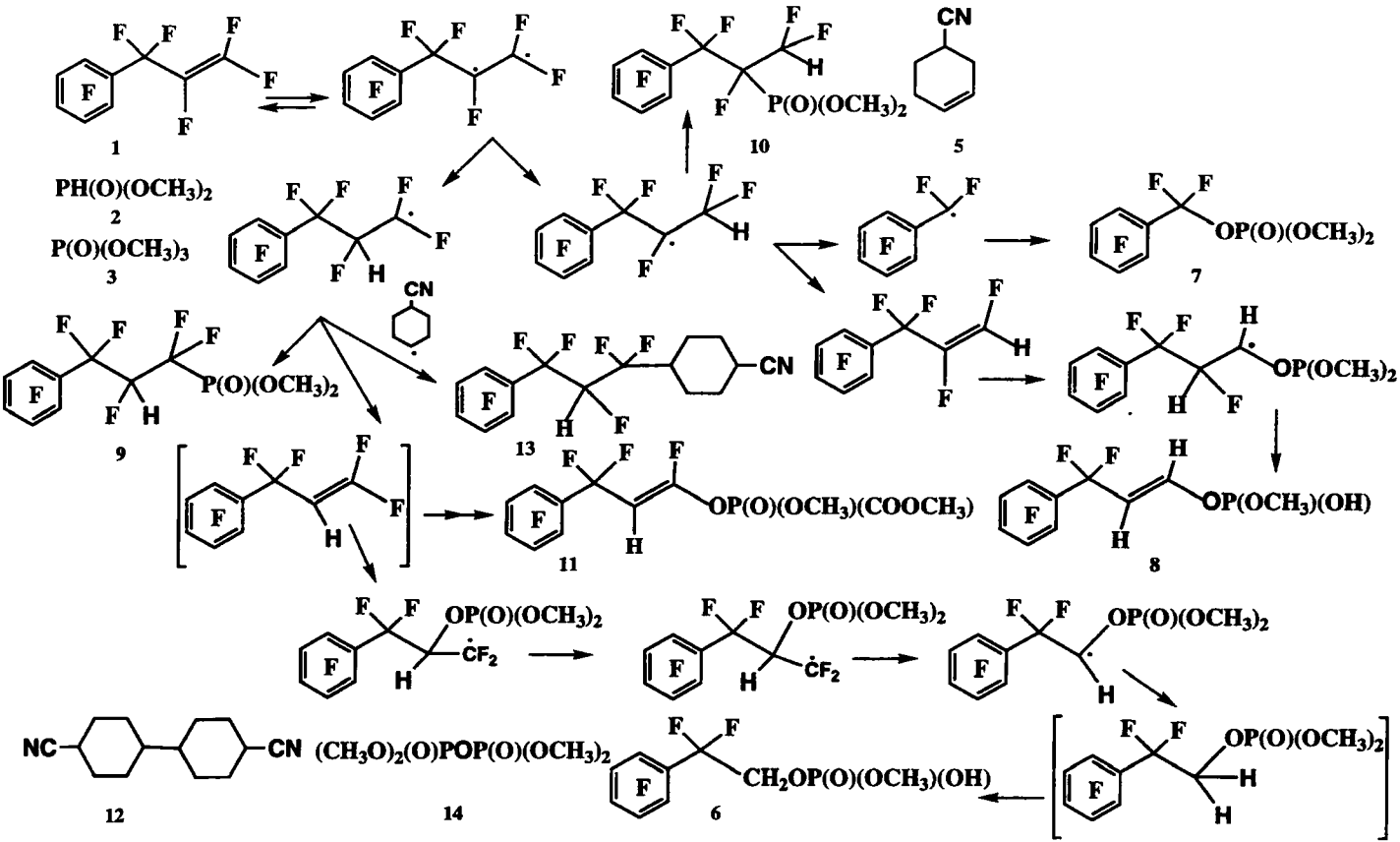

FIGURE 3 Probable mechanism of formation of compounds cited in Figure 1.

Elemental sulfur has been reacted with PFIB in the presence of SbF_5 via free radical intermediates.[16b] Recently, we described the reaction of PFIB with organometallics as well as with SO_3 in the presence of $B(OCH_3)$.[16c–d]

The photochemical reaction of PFIB (**15**, Figure 2) with hydrogen dimethylphosphonate (**2**) also gave 14 compounds, the structures of which have been elucidated using their mass spectral fragmentation behavior. The formation of [2-(trifluoromethyl)-3,3,3,1,1-pentafluoropropyl] dimethylphosphonate (**16**) can be rationalized on the basis of the addition of hydrogen and phosphonyl radicals to the carbon-carbon double bond. There are precedents for this.[17] In fact, the phosphonyl radical suggested here has been implicated as an intermediate in the thermal and photochemical formation of trimethyl phosphate.[15,18] Phosphine oxides have found industrial application as photo-initiators, thus showing that they are also photo-active.[19] The addition of the phosphonyl radical to the perfluoropropyl radical does not appear to pose any steric problem. Dimethyl hexafluoroisopropyl phosphonate **17** is formed from the hexafluoroisopropyl radical, which arises from the loss of difluorocarbene from the parental biradical and which then goes on to react with the phosphonyl radical to yield compound **17**. (cf. Figure 4) It is conceivable that compound **18**, namely octafluoroisobutyl methyl ether, could have arisen from the reaction of the octafluoroisobutyl radical with methoxyl radical split off from either $PH(O)(OCH_3)_2$ or $P(O)(OCH_3)_3$. There are precedents for this suggestion.[19e]

The 1,2,2,2-tetrafluoroethyl radical formed from the octafluoroisobutyl radical, via migration of the CF_3 group and the loss of a carbene entity, reacts with the phosphonyl radical to furnish dimethyl 1,2,2,2-tetrafluoroethyl phosphonate (**19**), which undergoes dealkylation to yield a pair of isomeric phosphonic acids **26** and **27**. There are precedents for such dealkylation reactions.[4b–d] Hydrogen (trifluoromethyl) methylphosphonate **20** has its origin in **2**, from which the methoxy moiety has been replaced by the trifluoromethyl group. Figure 4 describes the probable mechanism of the formation of 1,1,1,3-tetrafluoroisopropenylphosphonate (**21**). Compounds **22** and **24** owe their origin to the presence of the octafluoroisobutyl radicals formed by the addition of hydrogen to PFIB and followed by the reaction with the phosphonyl radical. The latter, namely **24**, undergoes further modification. Incidentally the characterization of octafluoroisobutylphosphonate (**22**) directly lends support to the proposed presence of the phosphonyl radical in the reaction mixture. The tentative identification of dimethyl (2-trifluoromethyl)octafluoroisobutylphosphinate (**23**) requires some explanation. The formation of methyl dimethlphosphonate from methyl

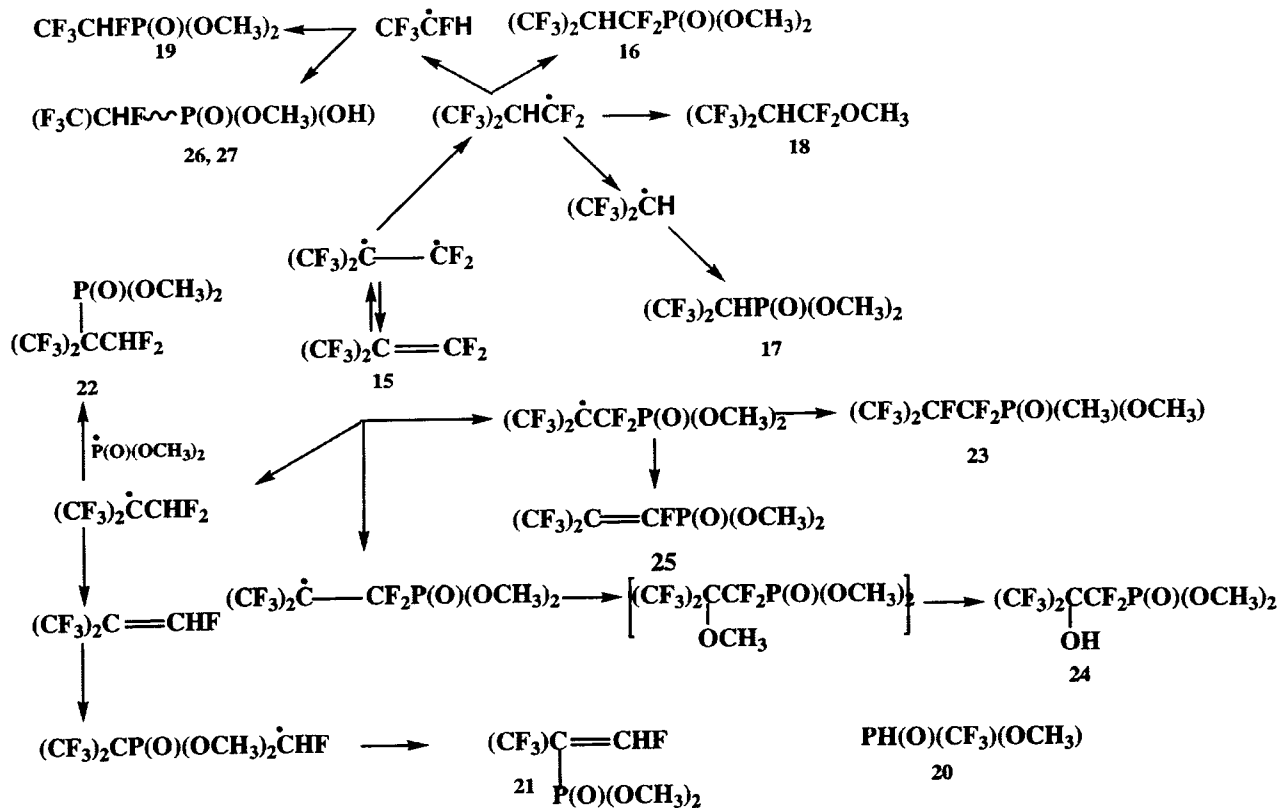

FIGURE 4 Probable mechanism of formation of compounds described in Figure 2.

radical and trimethylphosphite has been stated to be energetically favorable and the most likely source of dimethyl methylphosphonate may be the 'cross-combination' of methyl and phosphonyl radicals.[20] Dimethyl octafluoro(hydroxy)butylphosphonate (**24**) must have resulted from dimethyl methylphosphonyl radical, followed by the attack by the methoxy radical and loss of a methylene moiety from the methoxy group.

EXPERIMENTAL

Considerable care and caution should be exercized in handling and working with PFIB. Mass spectra were obtained using a Finnigan TSQ-7000 GC/MS/MS equipped with a 30 m × 0.25 mm. i.d. DB-5 capillary column (J and W Scientific, Folsom, CA) or a Finnigan 5100 GC/MS equipped with a 15 m × 0.25 mm. i.d. Rtx-5 capillary column (Restek, Bellefonte, PA). The conditions on 5100 were: oven temperature 60–270°C at 10°C/min, injection temperature was 210°, interface temperature 230°C, electron energy 70 eV, emission current 500 μA and scan time 1 sec. The conditions on the TSQ-7000 were: oven temperature 60–270°C at 15°C/min, injection temperature 220°, interface temperature 250°C, source temperature 150°, electron energy 70 eV (EI) or 200 eV (CI) and emission current 400 μA (EI) or 300 μA (CI) and scan time 0.7 sec. Data was obtained in both the electron ionization mode (range 45–450 da) and chemical ionization mode (mass range 60–450 da). Ultrahigh purity methane was used as the CI agent gas with a source pressure of 0.5 Torr (5100) or 4 Torr (TSQ-7100). Routine GC analyses were accomplished with a Hewlett-Packard 5890A gas chromatograph equipped with a J and W Scientific 30 m × 0.53 mm i.d. DB-5 column (J and W Scientific, Folsom, CA). 1H- and 13C-NMR spectra were recorded in CDCl3 on a Varian 200 (200 MHz) FT-NMR system.

MICROWAVE CATALYZED REACTION OF 3-(PERFLUOROPHENYL)PENTAFLUOROPROPENE (1, FIGURE 1) WITH HYDROGEN DIMETHYLPHOSPHONATE (2)

A solution of stoichiometric amounts 3-(perfluorophenyl)pentafluoropropene (**1**, 2.98 g, 0.01 mole), hydrogen dimethylphosphonate (**2**, 1.10 g, 0.01 mole) and 4,4′-azobis(cyclohexanecarbonitrile) (**4**) (25–35 mg) were mixed in a closed glass vial and reacted in a microwave (power set at

80%) for 2 minutes at a time up to a total of 4 minutes. The GC analysis of the reaction mixture showed it to consist of a very complex mixture of compounds. However, the GC-MS analysis of the reaction mixture permitted the elucidation of the structure of 14 compounds, some arising from the reaction of the free radical initiator itself. Thus (cf. Figure 4): (1) 3-(Perfluorophenyl)pentafluoropropene (**1**, r.t. = 2.24 min, 55.6%); M^+ = 298, 100%); 279 (M–F); 248 (M–CF_2); 229 (M–CF_3); 217 (M–C_2F_3, 96%); 198 (217-F); 179 (198-F); 167 (M–C_3F_5); 168 (C_6F_4); 131 (C_3F_5); 117 (148-F); 93 (C_3F_3) and 69 CF_3); (2) Hydrogen dimethylphosphonate (**2**, r.t. = 2.43 min, 31.8%); M^+ = 110; 109 (M–H); 95 (M–CH_3); 81 [PH_3(O)(OMe)]; 80 (81-H, 99%); 79 [PH(O)(OMe)]; 79 [PH(O)(OMe), 100%]; 65 [PH(O)(OH)]; 49 (PH_2O) and 47 (PO); (3) Trimethylphosphate (**3**, r.t. = 3.41 min, 1.1%); M^+ = 140; 110 (M–OCH_2, 100%); 109 (M–OMe]; 95 [P(O)(OH)(OMe)]; 79 (110-OMe); 65 (PH_2O_2) and 47 (PO); (4) 4,4′-Azobis(cyclohexanecarbonitrile), (**4**, r.t. = 4.24 min, 1.25%); M^+ = 218 (splits off into N_2 and 4-cyanocyclohexyl radical (108) which abstracts hydrogen to give cyanocyclohexane, M^+ = 109; 107 (C_7H_9N); 94 (109-CH_3, 100%); 81 (C_6H_9); 69 (C_5H_9); 67 (C_5H_7); 57 (C_4H_9); 56 (C_4H_8, 100%); 54(C_4H_6) and 53 (C_4H_5); (5) 4-Cyanocyclohexene, (**5**, r.t. = 4.7 min, 0.5%); M^+ = 107; 106 (M–H); 92 (M–CH_3, 100%); 80 (C_6H_8); 79 (C_6H_7); 77 (C_6H_5); 67 (C_5H_7); 65 (C_5H_5); 54 (C_4H_6) and 52 (C_4H_4); (6) Methyl [(perfluorobenzyl)methyl]phosphonic acid (**6**, r.t. = 5.01 min, 0.2%); M^+ = 342; 217 (C_7F_7, 100%); 198 (217-F); 167 (C_6F_5); 148 (167-F); 117 (167-CF_2); and 69 (CF_3); (7) Dimethyl perfluorobenzylphosphonate (**7**, r.t. = 6.2 min, 0.1%); M^+ = 342; 217 (C_7F_7, 100%); 198 (217-F); 179 (198-F); 167 (C_6F_5); 149 (167-F); 117 (167-CF_2); 79 79 [PO_3 or PH(O)(OMe)] and 69 (CF_3); (8) Methyl 2-(perfluorobenzyl)ethylene phosphonic acid (**8**, r.t. = 6.71 min, 0.25%); M^+ = 338; 217 (C_7F_7); 198 (217-F); 179(198-F); 167 (C_6F_5); 149 (167-F); 121 [C_2H_2P(O)(OH)(OMe), 100%]; 93 (CH_2PO_3) and 69 (CF_3); (9) Dimethyl-3-(perfluorophenyl)-1,1,2,3,3-pentafluoropropyl) phosphonate (**9**, r.t. = 8.21 min, 0.3%); M^+ = 408; 280 [M–F–P(O)$(OMe)_2$]; 261 (280-F); 241 [C_3HF_6 P(O)$(OMe)_2$]; 230 (180-CF_2); 217 (C_7F_7); 167 (C_6F_5); 131 ((C_3F_5); 109 [P(O)$(OMe)_2$, 100%]; 93 (109-CH_4); 79 (PO_3); 69 (CF_3); 63 (PO_2) and 51 (CF_2H); (10) Dimethyl 2-[(3-perfluorophenyl)-1,1,2,3,3-pentafluoropropyl] phosphonate(**10**, r.t. = 8.55 min, 2.9%); M^+ = 408; 391 (M-F); 307 [M-(C_2HF_4)]; 291 (307-CH_4); 280 [M–F–P(O)$(OMe)_2$]; 161 (280-F); 217 ($C_6F_5CF_2$); 179 (C_2HF_3 P(O)$(OMe)_2$]; 167 (C_6F_5); 131 ((C_3F_5); 109 [P(O)$(OMe)_2$, 100%]; 93 (109-CH_4); 79 (PO_3); 69 (CF_3); 63 (PO_2) and 47 (PO); (11) Carbomethoxy methyl [3-perfluorophenyl)-1-propenyl]phosphonate (**11**, r.t. = 9.94 min, 0.4%); M^+ = 414; 383 (M–OMe); 286 [M–F–P(O)$(OMe)_2$]; 217

($C_6F_5CF_2$); 197 [$C_2HFP(O)(OMe)_2$]; 167 (C_6F_5); 141 [$(P(OH)P(OMe)_2$]; 109 [$P(O)(OMe)_2$, 100%]; 93 (109-CH_4) and 79 (PO_3); (12) 4,4'-Dicyanodicyclohexane, (**12**, r.t. = 11.61 min, 3.9%); M^+ = 216 (not seen); 109 ($C_7H_{11}N$, 100%); 94 (109-CH_3); 82 [(109-HCN) or C_6H_{10}]; 67 (C_5H_7) and 53 (C_4H_5); (13) (4-Cyanohexyl)-(3-perfluorophenyl)-1,1,2,3,3,-pentafluoropropane (**13**, r.t. = 10.47, min, 0.5%); M^+ = 407; 217 ($C_6F_5CF_2$, 100%); 190 [$C_2HF_3C_6H_{10}CN$]; 170 (190-HF); 167 (C_6F_5); 108 [C_6H_8CN]; 81 [(108-HCN) or C_6H_9); 79 (C_6H_7) and 53 (C_4H_8); (14) Tetramethlpyrophosphate (**14**, r.t. = 13.45 min, 1.4%); M^+ = 234; 219 (M–CH_3); 193 (C_3H_7); 179 (193-CH_2); 151 [$P(OH)(OMe)_3$]; 100%); 111 [$PH(OH)(OMe)_2$] and 83 (H_4PO_3).

PHOTO-REACTION OF PERFLUOROISOBUTYLENE (15) WITH HYDROGEN DIMETHYLPHOSPHONATE (2)

A solution of stoichiometric amounts perfluoroisobutylene (**15**, 2.0 g, 0.0I mole), drawn through the vacuum line at −80°C and hydrogen dimethylphosphonate (**2**, 1.10 g, 0.0I mole) in dry pentane (5 ml) in a 10 ml three-necked round-bottom flask carrying dry ice-acetone cooled Dewar condenser was irradiated with a GE-100 Watt mercury lamp for 30 minutes after the reaction mixture had came to ambient temperature. The routine GC analysis showed it to be a complex mixture. The GC-MS analysis of the reaction mixture indicated the presence of 14 components, the structures of which have been elucidated by the examination of their mass spectral fragmentation behavior. Thus (cf. Figure 2): (a) Perfluoroisobutylene (**15**, r.t. = 1.26 min; 0.4%) M^+ = 210. We have previously described its mass spectrum[16c–d]; (b) (2-Trifluoromethyl)pentafluoroethyl dimethylphosphonate (**16**, r.t. = 1.28 min, 1.4%); M^+ = 310 (not seen); 201 [M–$P(O)(OMe)_2$]; 181 (201-HF); 132 (201-CF_3); 113 (132-F); 112 (113-H); 93 [112-F or $CH_3P(O)(OMe)$]; 82 (C_2HF_3); 69 (CF_3, 100%); 63 (PO_2) and 51 (CHF_2); (c) (1,1,1,3,3,3-Hexafluoro)isopropyl dimethylphosphonate (**17**, r.t. = 1.30 min,2.6%); M^+ = 260 (not seen); 198 [M-$(OMe)_2$]; 179 (198-F); 159 (179-HF); 150 [$C(CF_3)$]; 132 (179-PO); 113 (132-F); 110 (179-CF_3); 100 (C_2F_4); 82 (C_2HF_3); 69 (CF_3, 100%); 51 (CHF_2); and 47 (PO); (d) [2-(Trifluoromethyl)-1,1,3,3,3-pentafluoromethyl methyl ether (**18**, r.t. = 1.46 min, 7.5%); M^+ = 232 (not seen); 213 (M–F); 201 (M–OMe); 181 (213-MeOH); 179 (213-CH_3–F); 159 (179-HF); 144 (179-F–O); 132 (210-(CF_3); 113 (132-F); 93 (113-HF); 91 (179-CF_3–F); 81 (CF_2OMe, 100%); 69 (CF_3, 100%); and 47 (PO); (e) (1,1,1,2-Tetrafluoro)-ethyl dimethylphosphonate (**19**, r.t. = 1.60 min, 3.1%); M^+ = 210;

190 (M–HF); 179 (M–OMe, 100%); 170 (190-F); 159 (179-HF); 150 (170-HF); 111 [$CF_2CPH(OH)$]; 100 (C_2F_4); 93 [$P(O)CH_3OMe$]; 81 [$PH_3(O)(OMe)$]; 69 (CF_3); 63 (PO_3); 59 (CPO) and 51 (CHF_2); (f) Hydrogen (trilfuoromethyl) methylphosphinate (**20**, r.t. = 1.81 min, 3.0%); M^+ = 148; 99 (M–F–OCH_2); 98 (M–CF_2); 97 (M–F–MeOH); 83 (M–CF_2–CH_3); 80 (99-F); 69 (PHFO, 100%); 63 (PO_2); 50 (CF_2) and 47 (PO); (g) 1,1,1,2-Tetrafluoroisopropenyl) dimethylphosphonate (**21**, r.t. = 1.95 min, 2.3%); M^+ = 212; 193 (M–F); 181 (M–OMe); 178 (193-CH_3); 159 (178-F, 100%); 150 (181-OMe); 113 (C_2HF_4); 112 (CF_3C_2H); 100 (150-CF_2); 81 [$PH_3(O)(OMe)$]; 69 (CF_3) and 47 (PO); (h) Hydrogen dimethylphosphonate (**2**, r.t. = 2.43 min, 76.5%); M^+ = 110; 109 (M–H); 95 (M–CH_3); 81 [$PH_3(O)(OMe)$]; 80 (81-H, 99%); 79 [PH(O)(OMe)]; 79 [PH(O)(OMe), 100%]; 65 [PH(O)(OH)]; 49 (PH_2O) and 47 (PO); (i) 2-(Trifluoromethyl) 1,1,3,3,3-pentafluoro-2-propyl dimethylphosphonate (**22**, r.t. = 5.08 min, 0.01%); M^+ = 310; 280 (M–OMe); 249 (280-OMe); 211 (280-CF_3); 207 [$CF_3CCFP(O)(OH)$-(OMe)]; 159 [$CF_2P(O)(OMe)_2$]; 113 (182-CF_3); 97 [H_3PO_2(OMe)]; 93 (113-HF or $P(O)CH_3OMe$); 81 [$PH_3(O)(OMe)$]; 80 (81-H, 100%); 69 (CF_3); 63 (PO_3); 49 (PH_2O) and 47 (PO); (j) Hydrogen methyl [2-(trifluoromethyl)-1,1,3,3,3-pentafluoropropyl dimethylphosphinate (**23**, r.t. = 5.46 min, 0.3%); M^+ = 312; 293 (M–F); 282 (M–OCH_2); 253 (293-2HF); 244 (282-HF–H_2O); 201 (C_4HF_8); 181 (C_4F_7); 150 (C_3F_6); 132 (C_3HF_5); 113 (C_2HF_4); 109 [$P(O)(OMe)_2$]; 97 (CH_6PO_3); 94 (CH_3PO_3, 100%); 79 (PO_3); 69 (CF_3); 63 (PO_3); 49 (PH_2O); and 47 (PO); (k) 2-Hydroxy-2-(trifluoromethyl)-1,1,3,3,3,-pentafluorodimethylphosphonate (**24**, r.t. = 5.64 min, 0.7%); M^+ = 326; 307 (M–F); 296 (M–OCH_2); 287 (307-HF); 278 (M–OCH_3–OH); 201 (C_4HF_8); 181 (C_4F_7); 159 [$CF_2P(O)(OCH_3)_2$]; 132 (201-CF_3); 126 [$CH_3PH(OH)(OMe)_2$]; 113 (132-F); 109 [$P(O)(OMe)_2$]; 96 [PH(O)(OH) (OMe), 100%]; 95 [P(O)(OH)(OMe)]; 79 (PO_3 or PH(O OMe); 69 (CF_3) and 47 (PO); (l) Perfluoroisobutenyl dimethylphosphonate (**25**, r.t. = 5.85 min, 0.8%); M^+ = 290 (not seen); 271 (M–F); 259 (M–OMe); 221 (M–CF_3); 176 (221—CH_3–CH_2); 109 [$P(O)OMe)_2$]; 93 [P(O)(CH_3)(OMe), 100%]; 79 (PO_3 or PH(O OMe) and 47 (PO); (m) Methyl tetrafluoroethyl phosphonic acid (**26**, r.t. = 6.09 min, 0.9%); M^+ = 196 (not seen); 179 (M–OH); 157 [$C_2F_2P(O)(OH)(OMe)$]; 140 (157-OH); 110 [CHFP(O)(OMe), 100%]; 109 (110-H); 95 [P(O)(OH) (OMe)]; 79 [PO_3 or PH(O)(OMe)]; 69 (CF_3); 65 [PH(O)(OH)] and 47 (PO); (n) Methyl tetrafluoroethyl phosphonic acid (**27**, r.t. = 6.14 min, 1.0%); M^+ = 196 (not seen); 179 (M–OH); 129 [$C_2F_4P(O)$]; 110 [CHFP(O)(OMe); 109[CFP(O)(OMe), 100%]; 91 (110-F); 79 [PO_3or PH(O)(OMe)]; 69 (CF_3) and 47 (PO).

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