Free Radical Reaction of α-Haloalkylphosphonates with Alkenes and Alkynes: A New Approach to Modified Phosphonates[1]

Piotr Bałczewski, Marian Mikołajczyk*

Center of Molecular and Macromolecular Studies, Polish Academy of Sciences, Department of Organic Sulfur Compounds, 90-363 Łódź, Sienkiewicza PL-112, Poland

Fax + 48 (42) 847126

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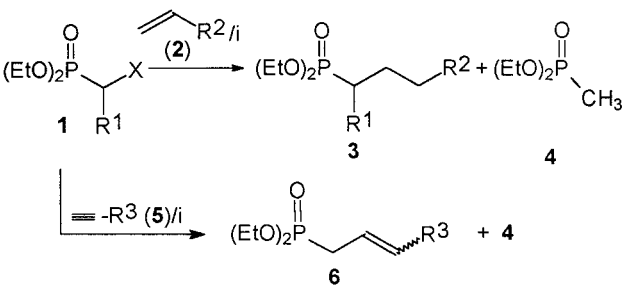
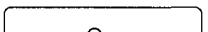
A new approach to the synthesis of phosphonates **3** functionalized in the α- and γ-phosphonate positions by alkyl, ethoxy, butoxy, acetoxy, acetyl and cyanide groups and allylphosphonate **6** is described. It is based on the radical reaction of α-halosubstituted phosphonates **1** (X = Cl, Br, I) with the terminally unsubstituted alkenes **2** (1-heptene, ethoxyethene, butoxyethene, acetoxyethene, acrylonitrile, methyl vinyl ketone) and alkyne **5** (hept-1-yne). The reaction involving the tin hydride method (Bu_3SnH/AIBN) was more effective with alkenes than with alkynes (40–72% versus 20–30%). With electron- rich alkenes, chloro- and bromomethylphosphonates **1** (X = Cl, Br) gave higher yields than iodomethylphosphonate **1** (X = I). Diethyl methylphosphonate **4**, as a reduction product of **1**, accompanied **3** and **6** in the above reactions. The yield of **4** could be reduced by optimizing the reaction conditions.





Scheme 1

Interest in phosphonates has been stimulated by recognition that they can be utilized in many areas such as biochemistry, medicine, organic synthesis, technique and plant protection.[2] The numerous methods for the synthesis of functionalized phosphonates may be divided into two main groups: the first involves C–P bond formation (the Arbuzov and Michaelis–Becker reactions), and the second one involves C–C and C–heteroatom bond formation (reactions of α-phosphonate carbanionic and electrophilic species with single and multiple carbon–carbon, carbon–heteroatom and heteroatom–heteroatom bonds).[3] These methods, however, suffer from a lack of generality and from that point of view every new synthesis of phosphonates is welcome in organic synthesis. In the Arbuzov reaction, for instance, aryl halides or tertiary aliphatic halides fail to react with phosphites. On the other hand, reactions involving addition of α-phosphonate carbanions to olefins and acetylenes are restricted to activated substrates only. In the case of bifunctional electrophiles, e.g. α,β-unsaturated carbonyl compounds, the carbanionic methods bring additional problems connected with the required stereoselectivity (1,2-versus 1,4-addition).[4] However, the recent improvements in regio- and stereoselectivity of radical reactions[5] enables some of these drawbacks to be overcome. Utilizing this new potential of radical chemistry, with its inherent advantages, we harnessed it to the synthesis of modified phosphonates **3** and **6**. In this paper, we present a radical addition reaction of α-phosphorylalkyl radicals **7** derived from α-halophosphonates **1** (X = Cl, Br, I) to electron-rich and -deficient alkenes **2** and alkyne **5** (Scheme 1).

Although α-phosphonyl radicals have so far been synthesized as adduct radicals in the radical addition reaction to vinylphosphonates,[6] our method presents a direct generation of the α-phosphorylalkyl radicals **7** from α-halophosphonates using the tin and silicon hydride method.[7] A selection in the first approach of the three α-unsubstituted and one α-methyl-substituted radical precursors **1** was connected with model studies and optimalization of the reaction conditions.

In the reaction of **1** with alkenes and alkynes under free radical conditions using tributyltin hydride/2,2'-azobisisobutyronitrile (Bu_3SnH/AIBN), two products containing phosphorus were formed in the ratios given in Table 1, i.e. the corresponding adducts **3**/**6** in 31–72% yield and diethyl methylphosphonate **4** as a reduction product of **1**. The two step process of separation and purification involved Kugelrohr distillation to remove the reduction product **4** and column chromatography over silica gel to remove tin salts. Bulky amounts of the tin salts, Bu_3SnX (X = CI, Br, I), were removed as insoluble Bu_3SnF by treatment with an aqueous solution of potassium fluoride. Formation of the phosphonates **3, 6** and **4** can be described by the four consecutive processes: (a) generation of the stannyl or silyl radicals, (b) generation of the α-phosphorylalkyl radical **7**, (c) formation of the adduct radicals, and (d) reduction of the formed radicals by R_3MH. Due to rather small differences in selectivity between the substrate and the adduct radicals in process (d), our efforts, as described in this paper, focused on optimalization of the **3/6:4** ratios.

An inspection of Table 1 shows that lesser amounts of the reduction product **4** and better yields of the adducts **3** were obtained when electron-rich alkenes (1-heptene, butoxyethene) were reacted with chloro- or bromometh-

Table 1. Free Radical Reaction of Diethyl α-Haloalkylphosphonates **1** with Alkenes **2** and Alkyne **5**

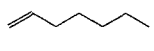
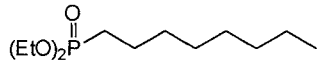
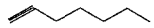
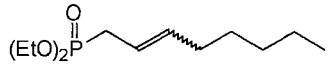
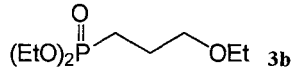
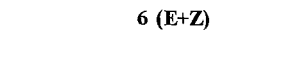
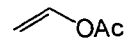
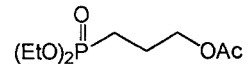
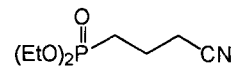
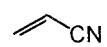
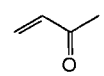
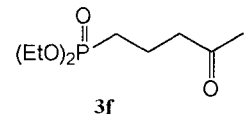
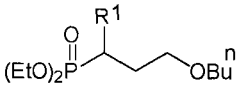
Phosphonate **1**[a]	Alkene **2**/Alkyne **5**	Amount of **2/5** (equiv)	Method	Product **3/6**	Ratio **3/6 : 4**	Yield **3/6** (%)
Cl		10	B		1 : 1.74	34
Br		5	A		1 : 1.83	34
		10	A	**3a**	1 : 0.89	53
		10	C		no 6	72
I		10	B		1 : 2.27	29
Cl		10	A		1 : 3.7	10
Br		10	D		1 : 2.4	22
				6 (E+Z)		
I		10	B		1 : 3.20	20
		10	D		1 : 1.6	31
Cl		10	A	 **3b**	1 : 1.11	42
Cl		3	A		1 : 1.96	32
		10	A		1 : 0.89	47
		10	E	**3c**	1 : 0.42	47
		10	A		1 : 0.35	49
		10	F		1 : 0.37	55
Br		10	A		1 : 1.15	32
I		10	G		1 : 5.3	13
		30	G		1 : 1.45	20/40[b]
Cl		10	B		1 : 0.62	62
						
I		10	A	**3d**	1 : 0.27	72
		10	B		1 : 0.71	58
Cl		10	A		1 : 0.43	39
						
Br		10	A	**3e**	1 : 0.17	64
I		3	A		1 : 0.8	40
		10	B		1 : 0.29	34
Br		10	A		1 : 0.8	39
				3f		

Table 1. (continued)

Phosphonate **1**[a]	Alkene **2**/Alkyne **5**	Amount of **2/5** (equiv)	Method	Product **3/6**	Ratio **3/6 : 4**	Yield **3/6** (%)
Cl		10	A	 **3g**	1 : 1.43	37

[a] R^1 = H (**3a–3f, 6**); R^1 = Me (**3g**).
[b] Yield based on material consumed.

ylphosphonates **1** (X = Cl, Br) rather than with iodomethylphosphonate **1** (X = I). With electron-deficient alkenes (acrylonitrile, methyl vinyl ketone) yields of **3** were generally worse, an exception being the reaction between **1** (X = Br) and acrylonitrile, for which 64% yield of **3c** was obtained.

Manipulation of stoichiometry of these reactions resulted in the finding that excesses of alkene or alkyne (5–10 equivalents) should be employed for optimal yields. On the other hand, the use of more than 30 equivalents is not recommended due to formation of byproducts. The three-fold excess of the phosphonate **1** (X = I) over butoxyethene resulted in total reduction and formation of **4** (100% yield). Quantitative yield of **4** was also obtained when **1** (X = Br) was reduced with Bu_3SnH/AIBN without a presence of alkene. The use of an insufficient amount of Bu_3SnH, such as to leave 5–20% of **1** (X = I) after completion of the reaction, significantly improved the **3/4** ratio. Thus, the phosphonate **1** (X = I) and acetoxyethene gave **3d/4** 1 : 0.71 compared to 1 : 0.27 (7.5% of **1** left). Similar results were obtained for **1** (X = Cl) and butoxyethene (**3c/4** 1 : 0.9 compared to 1 : 0.36, respectively). The increase of the addition time from 4 to 24 hours using the syringe pump technique did not change the yield of **3** and the **3/4** ratios. On the other hand, this technique brought only a several percent better yield of **3** in comparison with the conventional dropwise addition. The reactions were usually performed in a benzene or toluene solution. In benzene the reactions were more selective and lesser amounts of the reduction product **4** were observed. Thus, for **1** (X = Cl) and butoxyethene, the **3c/4** ratio was 1 : 0.42 in benzene versus 1 : 0.89 in toluene. We also examined other solvents and noticed, for instance, that in the case of reactive **1** (X = I) and butoxyethene, the use of a low boiling solvent such as cyclopentane allowed improvement in the yield and the **3c/4** ratio in comparison with the less reactive **1** (X = Cl, Method G). In that case, however, some amounts of **1** were left unreacted. The influence of concentration on the yields of **3/6** was not explicit. In some cases the 2- or 3-fold dilution (Method B versus A) only slightly improved yields of **3**. In the other cases, much better yields were reported for more concentrated solutions, especially in the case of hept-1-ene and hept-1-yne (Method C versus A) but in general higher concentrations might cause formation of side products other than **4**.

We found that the use of tris(trimethylsilyl)silane [$(Me_3Si)_3SiH$] did not improve the yield of **3** or the **3/4** ratio. Because of this and the higher cost of this hydride in comparison with Bu_3SnH, we did not continue further investigations with it.

Finally, it is worth noting that our radical based approach to phosphonate synthesis allows the synthesis of the α-functionalized phosphonate **3g**. Its synthesis by the Arbuzov reaction is rather difficult.

In conclusion, we describe herein a direct synthesis of diethoxyphosphorylalkyl radicals **7** from α-haloalkylphosphonates **1** (X = Cl, Br, I; R^1 = H, Me) and their reaction with both electron-rich and -deficient alkenes **2** and alkyne **5**. The main features of this reaction are following: (a) the selectivities of α-phosphorylmethyl radicals **7** against the adduct radicals involved in the chain do not differ much from each other, (b) the reaction between radicals and nonradicals is faster than radical recombination since the corresponding products of the latter reaction were not detected. In particular, the relative difference in selectivity between the α-phosphorylalkyl radicals **7**, which should be rather electrophilic in nature due to the electron-withdrawing effect of diethoxyphosphoryl group,[8] and the nucleophilic adduct radicals (R^1 = OR^3; R^3 = ethyl, butyl, acetyl) is bigger than the difference between α-phosphorylalkyl radicals **7** and the adduct radicals (R^1 = acetyl, cyanide) of electrophilic character. Under these conditions, the necessary optimalization of the reaction parameters and reagents structure allowed moderate and good yields of phosphonates **3, 6** to be obtained, thus offering a new and alternative synthesis of this class of compounds which utilizes free radical intermediates. Further investigation on application of other α-phosphonyl radical precursors (SR, SeR, COOH) and their inter- and intramolecular radical reactions are currently under way.

All the reactions were performed in a glass apparatus that consisted of a two- or three-necked flask equipped with one or two reflux condensers connected to a nitrogen source and mineral oil bubbler, a septum with a 15-cm long needle connected through Teflon tubing (diameter = 1.5 mm) to a disposal syringe which was placed in a diffusion pump, and a Teflon-coated magnetic stirrer bar. Flash column chromatography was performed using Merck silica gel (60, 230–400 mesh) and a gradient of benzene or toluene with acetone. ^1H NMR and ^{31}P NMR spectra were recorded at 200, 300 and 81 MHz respectively. LR and HRMS spectra were performed at 70 eV in the EI or CI mode. Satisfactory microanalyses were obtained for **1** (X = Cl): C – 0.13, H + 0.03, Cl + 0.22; **1** (X = Br): C – 0.15, H + 0.17, P + 0.20.

Benzene, toluene, heptane and cyclopentane (analytical grade of purity) were used without purification or distilled over sodium for

comparison purposes. All the solvents were deaerated with stirring before use under vacuum and kept under nitrogen or argon. All the alkenes and alkyne were used without purification from freshly opened bottles (Aldrich).

Diethyl Chloromethylphosphonate (1, X = Cl):
Compound **1** was purchased from Aldrich or prepared according to the modified procedure of Kabachnik and Shepeleva[9] as follows.

PCl_3 (52.5 g, 0.38 mol) was mixed with dry methanal (7.5 g, 0.25 mol) in a glass ampoule (wall thickness > 2.5 mm, otherwise danger of explosion), frozen and sealed under vacuum. The ampoule was put in the stainless steel tube and heated in the heater at 190–200 °C for 3–4 h (originally 230–250 °C, up to 11.5 h). The excess of PCl_3 was distilled off under at. press. and the residue was distilled using a water pump. Two products were separated:
(1) $Cl_2P(O)CHCl_2$: $n_D^{20} = 1.4940$.
^{31}P NMR ($CDCl_3$): $\delta = 38.8$.
^1H NMR ($CDCl_3$): $\delta = 4.15$ (d, $J = 6.2$ Hz).
(2) $Cl_2P(O)CH_2Cl$: $n_D^{20} = 1.4976$ (Lit.[9]: $n_D^{20} = 1.4990$).
^{31}P NMR ($CDCl_3$): $\delta = 33.4$.
^1H NMR ($CDCl_3$): $\delta = 3.87$ (d, $J = 8.7$ Hz).

The latter (15.5 g, 0.083 mol) was added to dry EtOH (60 mL) at −15 °C and left overnight in the fridge. After evaporation of the excess EtOH, the residue was dissolved in CH_2Cl_2, washed with 20% aq K_2CO_3, dried ($MgSO_4$), filtered, evaporated and distilled to give **1** (X = Cl); yield: 10 g (58%), 95–98 °C/10 mmHg, $n_D^{20} = 1.4400$. [Lit.[9]: 101 °C/5 mmHg, $n_D^{20} = 1.4415$, Aldrich Cat.: 109–110 °C/10 mmHg, $n_D^{20} = 1.4400$].
^1H NMR ($CDCl_3$): $\delta = 1.36$ (t, $J = 7.1$ Hz), 3.54 (d, $J = 10.5$ Hz); 4.21 (dq, $J = 7.1$; 8.2 Hz).
^{31}P NMR ($CDCl_3$): $\delta = 19.6$.
^1H NMR ($CDCl_3$): $\delta = 1.27$ (t, 6H, $J = 7.1$ Hz); 3.48 (d, 2H, $J = 10.5$ Hz), 4.21 (dq, 4H, $J = 7.1$, 8.2 Hz).

Diethyl Bromomethylphosphonate (1, X = Br):
Preparation was according to the modified procedure of Crofts and Kosolapoff[10] as follows. Diethyl phosphite (58.14 g, 60 mL, 0.35 mol) and dibromomethane (74.31 g, 30 mL, 0.427 mol) were mixed together in a glass ampoule (wall thickness > 2.5 mm) and sealed under vacuum. The ampoule was placed in the stainless steel tube and heated in the heater at 140–150 °C for 4 h. Distillation of the reaction mixture through the Vigreux column afforded three compounds: (1) $(EtO)_2P(O)CH_2CH_3$ (12.87 g), bp 65 °C/0.2 mmHg; (2) $(EtO)_2P(O)CH_2P(O)(OEt)_2$ (2.6 g), bp 80–90 °C/2 mmHg; (3) **1** (X = Br); (8.18 g), bp 90–120 °C/0.21 mmHg.

Analytically pure **1** (X = Br) was obtained by redistillation: bp 106–108 °C/0.15 mmHg (Lit.[9]: 50 °C/0.06 mbar; Lit.[11]: 86 °C/0.1 mmHg), $n_D^{20} = 1.4605$ (Lit.[9]: $n_D^{20} = 1.4592$).
^{31}P NMR ($CDCl_3$): $\delta = 18.98$.
^1H NMR ($CDCl_3$): $\delta = 1.33$ (dt, 6H, $J = 7.1$, $J_{HP} = 0.6$ Hz); 3.25 (d, 1H, $J = 9.8$ Hz); 4.17 (dq, 4H, $J_{HH} = 7.1$, $J_{HP} = 8.2$ Hz).

Diethyl Iodomethylphosphonate (1, X = I):
Preparation was according to Ref. 11; yield: 50%, bp 88 °C/0.07 mmHg, $n_D^{20} = 1.5003$ (Lit.[12]: bp 96–99 °C/0.5 mmHg, $n_D^{20} = 1.5002$; Lit.[13]: 101 °C/0.7 mmHg; $n_D^{20} = 1.4975$).
^{31}P NMR ($CDCl_3$): $\delta = 20.69$.
^1H NMR ($CDCl_3$): $\delta = 1.34$ (dt, $J = 7.1$ Hz); 3.02 (d, $J = 10.5$ Hz), 4.13 (dq, $J = 7.1$).

Diethyl 1-Chloroethylphosphonate (1, X = Cl, R^1 = Me):
Preparation was from diethyl 1-hydroxyethylphosphonate according to Ref. 14; yield: 56%, $n_D^{30} = 1.4336$ (Lit.[14]: $n_D^{20} = 1.4355$).

Free Radical Addition of 1 to Alkenes 2 or Alkyne 5; General Procedure:
Method A: To a deaerated and refluxing solution of **1** (1 mmol) and alkene **2** (10 mmol, see Table I) or alkyne **5** (10 mmol) in benzene or toluene (30 mL), a solution of Bu_3SnH (1.2–1.5 mmol) and AIBN (33 mg, 0.2 mmol) in the same solvent (17 mL) was added by syringe pump technique over 3 or 4 h. The resulting solution was refluxed for additional 1 h. The solvent was evaporated and the residue distilled using Kugelrohr apparatus and then purified by column chromatography over silica gel to give **3** or **6**. Bulky amounts of the tin salts (Bu_3SnX) could be removed before chromatography as Bu_3SnF by stirring overnight with an EtOAc solution of the reaction mixture with aq KF (with the exception of **3d**). The workup and purification for methods B–G were carried out as above.

Method B: Procedure as for Method A, using **1** (1 mmol) in benzene (80 mL) Bu_3SnH (1.2–1.5 mmol) in benzene (40 mL)/AIBN (20%).

Method C: Procedure as for Method A, using **1** (1 mmol) in toluene (4 mL) Bu_3SnH (1.2–1.5 mmol) in toluene (5 mL)/AIBN (20%).

Method D: Procedure as for Method A, using **1** (1 mmol) in benzene (10 mL) Bu_3SnH (1.2–1.5 mmol) in benzene (5 mL)/AIBN (20%).

Method E: carried out in toluene with stoichiometry according to Method A.

Method F: carried out with $(Me_3Si)_3SiH$ (1.2–1.4 equiv) in benzene with stoichiometry according to Method A.

Method G: Procedure as for Method A, using **1** (1 mmol) in cyclopentane (160–200 mL) Bu_3SnH (1.2–1.5 mmol) in cyclopentane (80 mL)/AIBN (20%) dissolved in benzene (1.5 mL).

Diethyl Octylphosphonate (**3a**): $n_D^{20} = 1.4381$.
^1H NMR ($CDCl_3$): $\delta = 0.87$ (t, 3H, $J = 6.5$ Hz); 1.25–1.80 (m, 14H); 1.31 (t, 6H, $J = 7.1$ Hz); 4.08 (m, 4H).
^{31}P NMR ($CDCl_3$): $\delta = 33.3$.
MS (EI): m/z (%) = 250 (M^+, 6); 179 (17); 166 (15); 165 (37); 152 (100); 138 (21); 137 (16); 125 (45); 111 (16); 108 (12); 97 (10); 55 (4); 41 (10).
HRMS: Calc. for $C_{12}H_{27}O_3P$: 250.1697. Found: 250.1674.

Diethyl Oct-2-enylphosphonate (**6**): $n_D^{20} = 1.4497$; $E/Z = 1:1$.
^1H NMR ($CDCl_3$): $\delta = 0.85$ (2 t, 3H, $J = 6.7$ Hz), 1.29, 1.31 (2 t, 6H, $J = 7.0$ Hz); 1.20–1.40 (m, 4H); 1.50–1.85 (m, 2H); 1.97–2.12 (m, 2H); 2.52 (2H, ddd, $^2J_{HP} = 20.4$, $^3J_{H-H} = 7.0$, $^4J_{H-H} = 0.9$ Hz, *E* or *Z*); 2.57 (2H, ddd, $^2J_{H-P} = 21.6$; $^3J_{H-H} = 7.7$; $^4J_{H-H} = 0.7$ Hz, *Z* or *E*); 4.04 (m, 4H); 5.31–5.64 (m, 2H).
^{31}P NMR ($CDCl_3$): $\delta = 28.2$, 28.1 (*E*/*Z*).
MS (EI): m/z = 248 (M^+, 78), 205 (100), 152 (92), 138 (69), 111 (65).
HRMS: Calc. for $C_{12}H_{25}O_3P$: 248.1541. Found: 248.1536.

Diethyl 3-Ethoxypropylphsphonate (**3b**): $n_D^{20} = 1.4475$.
^1H NMR ($CDCl_3$): $\delta = 1.18$ (t, 3H, $J = 7.0$ Hz), 1.20–1.45 (m, 2H); 1.31 (t, 6H, $J = 7.0$ Hz); 1.55–1.96 (m, 2H); 3.44 (t, 2H, $J = 6.1$ Hz); 3.45 (q, 2H, $J = 7.0$ Hz); 4.08 (m, 4H).
^{31}P NMR ($CDCl_3$): $\delta = 32.9$.
MS (EI): m/z (%) = 225 (M + 1, 33); 195 (34); 152 (33); 123 (57); 121 (22); 125 (47); 81 (22); 59 (23); 41 (53); 31 (49); 29 (20); 27 (58).
HRMS: Calc. for $C_9H_{22}O_4P$: 225.1255. Found: 225.1274.

Diethyl 3-Butoxypropylphosphonate (**3c**): bp 125 °C/0.4 mmHg (Kugelrohr): $n_D^{20} = 1.4453$.
^1H NMR ($CDCl_3$): $\delta = 0.89$ (t, 3H, $J = 7.1$ Hz); 1.30 (t, 6H, $J = 7.1$ Hz); 1.25–1.40 (m, 4H); 1.70–1.95 (m, 2H); 3.38 (t, 2H, $J = 6.5$ Hz); 3.42 (dt, 2H, $^3J_{H-H} = 6.0$, $^4J_{H-P} = 1.0$ Hz), 4.06 (m, 4H).
^{31}P NMR ($CDCl_3$): $\delta = 32.7$
MS (EI): m/z (%) = 253 (M + 1, 10); 195 (86); 152 (70); 151 (25); 125 (56); 123 (83); 121 (24); 81 (26); 65 (21); 42 (20); 41 (88); 29 (10); 27 (47).
HRMS: calc. for $C_{11}H_{26}O_4P$: 253.1573. Found: 253.1568.

Diethyl 3-Acetoxypropylphosphonate (**3d**): oil.
^1H NMR ($CDCl_3$): $\delta = 1.31$ (t, 6H, $J = 7.1$ Hz); 1.53–2.00 (m, 4H); 2.03 (s, 3H); 4.08 (m, 6H).
^{31}P NMR ($CDCl_3$): $\delta = 31.46$.

MS (EI): *m/z* (%) = 238 (M^+, 2); 195 (24); 179 (28); 152 (38); 151 (28); 125 (28); 123 (69); 109 (28); 43 (100).

HRMS: calc. for $C_9H_{19}O_5P$: 238.0969. Found: 238.0959.

Diethyl 3-Cyanopropylphosphonate **(3e)**: $n_D^{20} = 1.4444$.

^1H NMR ($CDCl_3$): $\delta = 1.33$ (t, 6, $J = 7.1$ Hz); 1.80–2.09 (m, 4H); 2.50 (dt, 2H, $^3J_{H-H} = 6.4$; $^4J_{H-P} = 0.7$ Hz); 4.11 (m, 4H).

^{31}P NMR ($CDCl_3$): $\delta = 30.08$.

MS (EI): *m/z* (%) = 205 (M^+, 10); 203 (100); 190 (20); 185 (44); 178 (27); 165 (84); 162 (48); 152 (49); 150 (92); 138 (64); 137 (30); 132 (84); 125 (52); 124 (20); 111 (31); 109 (71); 97 (28); 41 (37).

HRMS: calc. for $C_8H_{16}NO_3P$: 205.0867. Found: 205.0858.

Diethyl 4-Oxopentylphosphonate **(3f)**: oil.

^1H NMR ($CDCl_3$): $\delta = 1.32$ (t, 6H, $J = 7.0$ Hz); 1.48–1.95 (m, 6H); 2.14 (s, 3H); 2.58 (t, 2H, $J = 6.8$ Hz); 4.03–4.17 (m, 4H).

^{31}P NMR ($CDCl_3$): $\delta = 31.79$.

MS (EI): *m/z* (%) = 222 (M^+, 10); 180 (42); 179 (37); 177 (17); 165 (48); 152 (100); 151 (26); 149 (41); 138 (19); 137 (16); 125 (91); 123 (45); 109 (24); 108 (25); 47 (35); 67 (15); 43 (24).

HRMS: Calc. for $C_9H_{19}O_4P$: 222.1021. Found: 222.1017.

Diethyl 1-Methyl-3-butoxypropylphosphonate **(3g)**: $n_D^{20} = 1.4490$.

^1H NMR ($CDCl_3$): $\delta = 0.91$ (t, 3H, $J = 7.0$ Hz); 1.18 (dd, 3H, $^3J_{H-H} = 7.1$; $^2J_{H-P} = 19.3$ Hz); 1.31 (t, 6H, $J = 7.0$ Hz); 1.28–1.66 (m, 6H); 1.95–2.15 (m, 1H); 3.30–3.53 (m, 4H) 4.09 (dq, 4H, $^3J_{H-H} = {}^3J_{H-P} = 7.0$ Hz).

^{31}P NMR ($CDCl_3$): $\delta = 35.6$.

MS (EI): *m/z* (%) = 209 (42); 166 (100).

HRMS (CI): Calc. for $C_{12}H_{28}O_4P$: 267.1725. Found: 267.1715.

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(1) Phosphorus containing radicals. Part 1.
(2) Mastalerz, P. *Handbook of Organophosphorus Chemistry*; Engel, R., Ed.; Marcel Dekker: New York, Basel, Hong Kong; 1992, chapter 7, p 277.
Mikołajczyk, M.; Bałczewski, P. *Advances in Sulfur Chemistry*; Block, E., Ed.; Jai: 1994, pp 41–96.
Bałczewski, P.; Graczyk, P.; Perlikowska, W.; Mikołajczyk, M. *Tetrahedron* **1993**, *49*, 10111.
(3) Harvey, R.G.; DeSombre, E.R. *Topics in Phosphorus Chemistry*; Grayson, M.; Griffith, E.J., Eds.; Interscience: New York, vol. 1, 1964, p 58.
Kirby, A.J.; Warren, S.G. *Reaction Mechanisms in Organic Chemistry; Monograph 5, The Organic Chemistry of Phosphorus*; Eaborn, C.; Chapman, N.B.; Eds.; Elsevier: Amsterdam, London, New York, 1967.
(4) Mikołajczyk, M.; Bałczewski, P. *Tetrahedron* **1992**, *48*, 8697.
(5) *C-Radikale: Houben-Weyl*, 4th ed., Vol. E19; Regitz, M.; Giese, B., Eds.; Thieme: Stuttgart, 1989; Parts 1 and 2.
Jasperse, C.P.; Curran, D.P.; Fevig, T.L. *Chem. Rev.* **1991**, *91*, 1237.
Porter, N.A.; Giese, B.; Curran, D.P. *Acc. Chem. Res.* **1991**, *24*, 296.
Curran, D.P. *Synthesis* **1988**, 417, 489.
Giese, B. *Radicals in Organic Synthesis: Formation of Carbon–Carbon Bonds;* Pergamon; Oxford, 1986.
Beckwith, A.L.J. Chem. Soc. Rev. **1993**, 143.
(6) Baban, J.A.; Roberts, B.P. *J. Chem. Soc., Chem. Commun.* **1979**, 373.
Baban, J.A.; Roberts, B.P.; *J. Chem. Soc., Perkin Trans. 2.* **1981**, 161.
Barton, D.H.R.; Togo, H.; Zard, S.Z. *Tetrahedron Lett.* **1985**, *26*, 6349.
Baban, J.A.; Roberts, B.P. *J. Chem. Soc., Perkin Trans. 2*, **1988**, 1195.
Barton, D.H.R.; Gero, S.D.; Quiclet-Sire, B.; Samadi, M. *J. Chem. Soc., Chem. Commun.* **1989**, 1000.
Barton, D.H.R.; Gero, S.D.; Quicket-Sire, B.; Samadi, M. *Tetrahedron* **1992**, *48*, 1627.
(7) A single electron transfer mechanism with formation of difluoromethylphosphonyl radical was proposed by Burton for the palladium- or copper-initiated reactions of iododifluoromethyl phosphonates with alkenes; Yang, Z.-Yu.; Burton, D.J.; *J. Org. Chem.* **1992**, *57*, 4676. The same radical was prepared from diethyl bromodifluoromethylphosphonate and added to various alkenes under Co(III)/Zn bimetal redox conditions. Hu, Ch.-M.; Chen, J.; *J. Chem. Soc., Perkin Trans. 1* **1993**, 327.
(8) Creary, X.; Benage, B.; Mehrsheikh-Mohammadi, M.E.; Bays, J.P. *Tetrahedron Lett.* **1985**, *26*, 2383.
Luedtke, A.E.; Timberlake, J.W. *J. Org. Chem.* **1985**, *50*, 268.
(9) Kabachnik, M.J.; Shepeleva, E.S. *Izv. Ak. Nauk SSSR, Ser. Khim.* **1951**, 185; *Chem. Abstr.* **1951**, *45*, 10191.
(10) Crofts, P.C.; Kosolapoff, G.M. *J. Am. Chem. Soc.* **1953**, *75*, 5738.
(11) Coutrot, P.; Youssefi-Tabrizi, M.; Grison, C. *J. Organomet. Chem.* **1986**, *316*, 13.
(12) Cade, J.A. *J. Chem. Soc.* **1959**, 2266.
(13) Ford-Moore, A.F.; Williams, J.H. *J. Chem. Soc.* **1947**, 1465.
(14) Gajda, T. *Synthesis* **1990**, 717.