Addition of Diethyl Bromodifluoromethylphosphonate to Various Alkenes Initiated by Co(III)/Zn Bimetal Redox System

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The addition of diethyl bromodifluoromethylphosphonate **1** to various alkenes **2** initiated by cobaloxime(III)/Zn bimetal redox system gives 1:1 Michael-type adducts **3** in moderate to good yields. A radical mechanism is proposed.

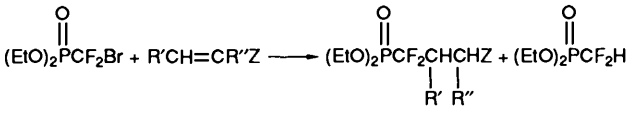
Phosphonates and their derivatives usually show significant biological activities, while selective substitution of fluorine atoms in such molecules often leads to pronounced enhancement of activity.[1] In recent years, synthesis of compounds containing a difluoromethylenephosphonate moiety has attracted much attention.[2] For example, Johnson synthesized 2-amino-7,7-difluoro-7-phosphonoheptanoic acid from diethyl difluoromethylphosphonate, and reported that such a fluorine-substituted acid showed a lower affinity than did its parent, unfluorinated analogue.[3] Kim reported the preparation of 9-(4,4-difluoro-4-phosphonobutyl)guanine and its antiviral activity was evaluated.[4] Chambers synthesized difluoromethylenephosphonyl-substituted compounds of biological interest.[5] The best approach to synthesize molecules containing a difluoromethylenephosphonate functionality is to utilize diethyl bromodifluoromethylphosphonate[6] as a starting material and its direct addition to various functionalized alkenes. However, until now, few efficient methods were available,[7] especially for the addition to electron-deficient alkenes

Owing mainly to the electrophilic nature of the fluorinated radicals, the addition of per(poly)fluoroalkyl halides to electron-deficient alkenes such as ethyl acrylate was not easy. Recently, we found that a bimetal redox system, cobaloxime(III)/Zn, could efficiently initiate the addition of per(poly)fluoroalkyl iodides or bromides to electron-deficient alkenes.[8] Herein we report the addition of diethyl bromodifluoromethylphosphonate to various alkenes, initiated by such a redox couple.

Results and Discussion

In the presence of bromo(pyridine)cobaloxime(III)/Zn bimetal redox system, the addition of diethyl bromodifluoromethylphosphonate **1** to electron-deficient alkenes **2** proceeded readily (Scheme 1). Generally, a mixture of a catalytic amount of cobaloxime(III) (0.1 mmol) and an excess of zinc powder (10 mmol) in ethanol was stirred under nitrogen for 30 min then a solution of phosphonate **1** (5 mmol) and alkene **2** (5.5 mmol) in ethanol was added dropwise to the mixture at 0 °C. After the mixture had been stirred at room temperature for several hours, usual work-up gave 1:1 hydro difluoro methylenephosphonation products **3**. The results obtained are summarized in Table 1. Solvents such as ethanol and tetrahydrofuran (THF) did not show any significant effect on this reaction (entries 1 and 2).

Such an addition proceeded smoothly with acrylic acid and its derivatives. No polymerized or telomerized product was found. Ethyl acrylate **2a** gave the corresponding adduct **3a** in 65% yield. Acrylic acid **2c** and its amide **2d** could also be a useful substrate in this reaction. When EtOH was used as solvent, acrylic acid **2c** gave the corresponding ethyl ester **3a**. It was obvious that the Co complex catalysed such an esterification. With methyl acrylate **2b**, a mixture of 80% ethyl ester **3a** and 20% methyl ester **3b** from Co complex-catalysed ester exchange was obtained in ~60% isolated yield. In THF, pure methyl ester **3b** was obtained in 62% isolated yield. Ethyl methacrylate **2e** gave satisfactory results, while ethyl crotonate **2f** gave a lower yield (34%) (entries 7 and 8). This was attributed to steric effects. The reaction also fitted well with acrylonitrile **2g** (67% yield) and α,β-unsaturated ketones such as methyl vinyl ketone **2h** (64% yield).



Scheme 1

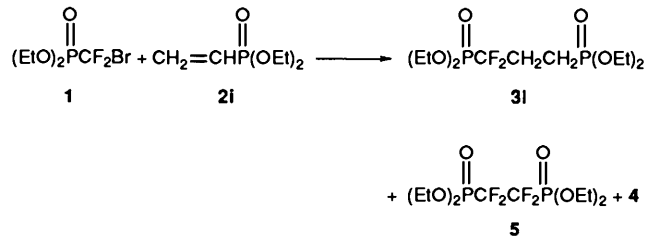
	R′	R″	Z
a	H	H	CO_2Et
b	H	H	CO_2Me
c	H	H	CO_2H
d	H	H	$CONH_2$
e	H	Me	CO_2Et
f	Me	H	CO_2Et
g	H	H	CN
h	H	H	Ac

Table 1 Addition of diethyl bromodifluoromethylphosphonate **1** to various alkenes **2** initiated by the Co^{III}/Zn redox system[a]

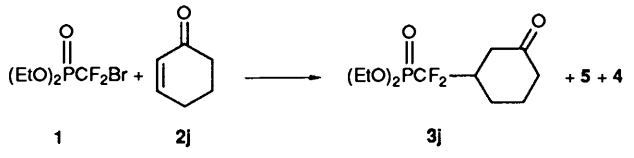
Entry	Alkene 2	Time (*t*/h)	Adduct 3	Yield (%)[b] of 3	By-product 5 or 6 (%)
1	**2a**	5	**3a**	65	
2	**2a**	6	**3a**	67[c]	
3	**2b**	5	**3a** + **3b**	60[d]	
4	**2b**	5	**3b**	62[c]	
5	**2c**	6	**3a**	53	
6	**2d**	8	**3d**	54	
7	**2e**	5	**3e**	72	
8	**2f**	10	**3f**	34	
9	**2g**	6	**3g**	67	
10	**2h**	9	**3h**	64	
11	**2i**	10	**3i**	35	**5** (10)
12	**2j**	12	**3j**	18	**5** (25)
13	**2k**	9	**3k**	58	**6** (18)
14	**2l**	10	**3l**	32	**6** (18)
15	**2m**	8	**3m**	52	
16	**2n**	6	**3n**	59	

[a] The solvent used was EtOH unless otherwise indicated. Molar proportions **1**:**2**:Co^{III}:Zn 1:1.1:0.02:2. [b] Isolated yield based on initial substrate **1**. Purification by distillation or column chromatography on silica gel. [c] The solvent used was THF. [d] A mixture of 80% ethyl ester **2a** and 20% methyl ester **2b** was obtained as estimated by ^1H NMR spectroscopy.

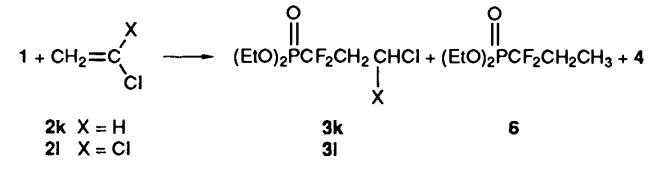
Diethyl vinylphosphonate **2i** could be used as acceptor, and a mixture of products **3i**, **4** and **5** was obtained. Bisphosphonate **5** was the coupling product of substrate **1**. Pure samples of compounds **3i** and **5** were obtained and characterized by mass, IR, ^{1}H NMR and ^{19}F NMR spectroscopy.



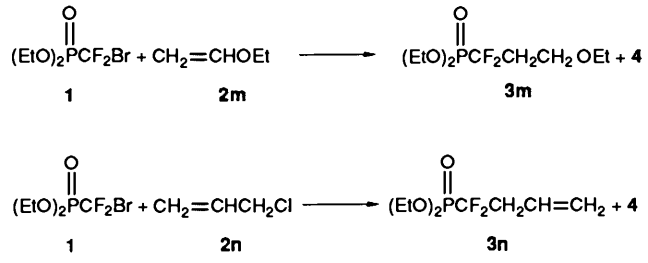
Cyclohex-2-enone **2j** gave similar results. However, only an 18% yield of compound **3j** together with a 25% yield of the coupling product **5** were obtained.



With vinyl chloride **2k** or vinylidene dichloride **2l** the corresponding 1:1 adduct **3k** or **3l** was obtained in moderate yield together with the same reduced product **6**. It is interesting to note that when dichloride **2l** was used as acceptor, no partially reduced product **3k** could be detected even by GC–MS.

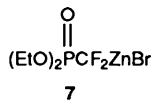


Such redox system could also effectively promote the addition of $(EtO)_2P(O)CF_2Br$ to electron-rich alkenes. Thus diethyl 3-ethoxy-1,1-difluoropropylphosphonate **3m** or diethyl 1,1-difluorobut-3-enylphosphonate **3n** could be easily obtained when ethyl vinyl ether **2m** or allyl chloride **2n** was respectively used as acceptor. This method thus provided a simpler way to synthesize diethyl 1,1-difluorobut-3-enylphosphonate.[5]

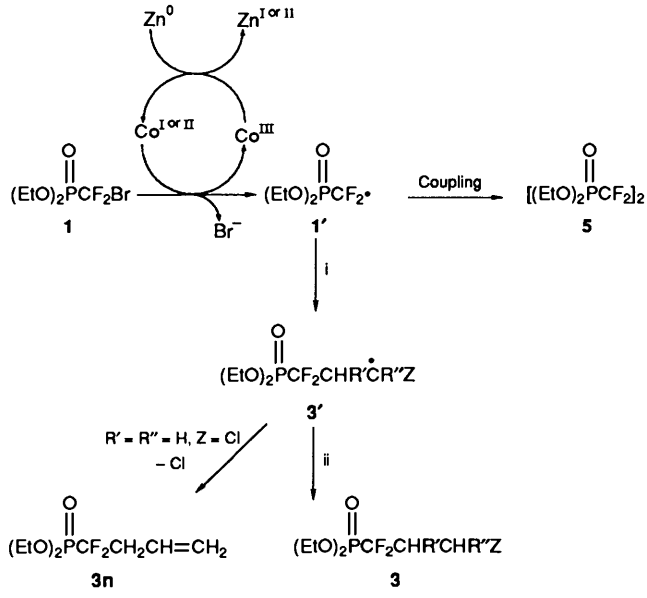


The main by-product in such addition reactions was diethyl difluoromethylphosphonate **4**.

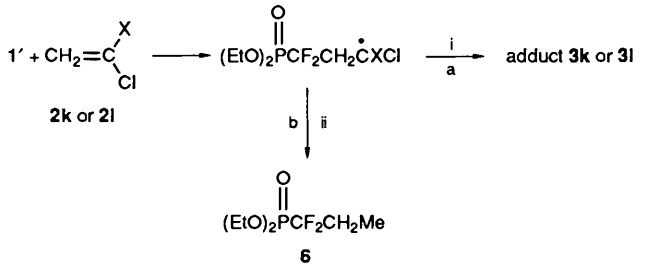
In the absence of a catalytic amount of Co(III) complex, no addition took place, and bromo compound **1** was converted into product **4** exclusively. Freshly prepared (diethoxyphosphoryl)difluoromethylzinc bromide **7** in THF or ethanol did not add to alkenes either in the presence or in the absence of cobaloxime(III) complex, but merely led to compound **4**.



Based on the above facts the following mechanism is logically proposed. The low-valent Co^I or Co^{II} species is the real initiator which promotes the radical addition of bromide **1** to alkenes **2** to form radical **3′**, which gives adduct product **3** by abstraction of a hydrogen atom. Such a cobaloxime catalyst can be recycled. With allyl chloride **2n**, the intermediate radical formed eliminates a β-chlorine atom to give product **3n**. In the case of substrates **2i** and **2j**, the radical **1′** partially coupled to give dimer **5** (Scheme 2). The formation of compound **6** could be attributed to the reduction of this intermediate by zinc (Route b in Scheme 3).



Scheme 2 *Reagents:* i, CHR′=CR″Z; ii, [H]



Scheme 3 *Reagents:* i, [H]; ii, Zn

Experimental

B.p.s are uncorrected. IR spectra were recorded on a Shimadzu IR-440 spectrometer. ^{1}H NMR spectra were measured using $SiMe_4$ as external standard on a Varian EM-360A spectrometer at 60 MHz or Varian XL-200 spectrometer at 200 MHz. ^{19}F NMR spectra were measured with external CF_3CO_2H (TFA) standard by a Varian EM-360 spectrometer at 56.4 MHz for samples in CCl_4 or $CDCl_3$ solution (upfield positive). Coupling constants are reported in Hz. Mass spectra were recorded on a Finnigan GC-MS-4021 mass spectrometer. All chemicals and reagents were of analytical grade and were used without further purification. Light petroleum refers to the fractions boiling in the range 60–90 °C.

Diethyl bromodifluoromethylphosphonate **1** was prepared

according to ref. 6. Bromo(pyridine)cobaloxime(III) was synthesized according to ref. 9.

General Procedure for the Addition of Bromide **1** *to Alkenes* **2**.—A mixture of bromo(pyridine)cobaloxime(III) (0.1 mmol) and zinc powder (10 mmol) in absolute ethanol (20 cm^3) was vigorously stirred at room temperature under N_2 for 30 min, during which period the colour of the suspension changed from brown to green. Then a solution of compounds **1** (5.0 mmol) and **2** (5.5 mmol) in EtOH (2 cm^3) was added dropwise to the mixture, and the whole contents were cooled with an ice–water-bath. The reaction conditions were as indicated in Table 1. After that the mixture was poured into ice–water (20 cm^3) and extracted with diethyl ether (3 × 20 cm^3). The combined extract was washed successively with saturated aq. $NaHSO_3$, water and brine, and was dried over Na_2SO_4. After removal of diethyl ether, the residue was purified by distillation under reduced pressure or through column chromatography on silica gel with light petroleum–ethyl acetate mixture (99:1 or 1:1) as eluant to give pure products **3**.

Ethyl 4-(*diethoxyphosphoryl*)-4,4-*difluorobutyrate* **3a**. B.p. 135–137 °C/3 mmHg (Found: C, 41.5; H, 6.7. $C_{10}H_{19}F_2O_5P$ requires C, 41.67; H, 6.60%); ν_{max}(neat)/cm^{-1} 1735s (C=O), 1280s (P=O), 1180s (C–F) and 1020s; δ_H 4.3 (6 H, m), 2.0–2.8 (4 H, m) and 1.36 (9 H, $^3J_{HH}$ 7); δ_F 34.0 (CF_2, dt, $^2J_{PF}$ 115, $^3J_{HF}$ 21); *m/z* 289 (M + 1, 100%) and 243 (M − OEt, 72).

Methyl 4-(*diethoxyphosphoryl*)-4,4-*difluorobutyrate* **3b**. B.p. 111–112 °C/2 mmHg (Found: C, 39.4; H, 6.2. $C_9H_{17}F_2O_5P$ requires C, 39.42; H, 6.20%); ν_{max}(neat)/cm^{-1} 1725s (C=O), 1260s (P=O), 1140s (C–F) and 1020s; δ_H 4.34 (4 H, dq, $^4J_{HP}$ 10, $^3J_{HH}$ 7), 3.7 (3 H, s), 1.8–2.9 (4 H, m) and 1.42 (6 H, t, $^3J_{HH}$ 7); δ_F 36.0 (CF_2, dt, $^2J_{PF}$ 115, $^3J_{HF}$ 21); *m/z* 275 (M + 1, 100%) and 243 (M − OMe, 52).

4-(*Diethoxyphosphoryl*)-4,4-*difluorobutyramide* **3d** (Found: M^+, 259.0777. $C_8H_{16}F_2NO_4P$ requires *M*, 259.0781); ν_{max}(neat/cm^{-1} 3350s (NH_2), 1680s (C=O), 1280s (P=O), 1160m (C–F) and 1020s; δ_H 10.4 (2 H, br, NH_2), 4.2 (4 H, dq, $^4J_{PH}$ 10, $^3J_{HH}$ 7), 1.8–2.8 (4 H, m) and 1.36 (6 H, $^3J_{HH}$ 7); δ_F 34 (CF_2, dt, $^2J_{PF}$ 115, $^3J_{HF}$ 21); *m/z* 260 (M + 1, 100%), 243 (M − NH_2, 62.66), 223 (M − NH_2 −HF, 0.53), 215 (M − $CONH_2$, 4.75) and 187 (M − $CH_2CH_2CONH_2$, 3.74).

Ethyl 4-(*diethoxyphosphoryl*)-4,4-*difluoro*-2-*methylbutyrate* **3e**. B.p. 131–133 °C/1 mmHg (Found: C, 43.75; H, 6.7. $C_{11}H_{21}F_2O_5P$ requires C, 43.71; H, 6.95%); ν_{max}(neat)/cm^{-1} 1735s (C=O), 1280s (P=O), 1180m (C–F) and 1020s; δ_H 4.30 (6 H, m), 3.0 (3 H, m) and 1.38 (12 H, m); δ_F 33 (CF_2, dt, $^2J_{PF}$ 115, $^3J_{HF}$ 21); *m/z* 303 (M + 1, 1.51%), 257 (M − OEt, 100) and 229 (M − CO_2Et, 23).

Ethyl 4-(*diethoxyphosphoryl*)-4,4-*difluoro*-3-*methylbutyrate* **3f**. B.p. 110–112 °C/1 mmHg (Found: C, 43.7; H, 6.8%); ν_{max}(neat)/cm^{-1} 1740s (C=O), 1380m (CH_3), 1280s (P=O), 1160m (C–F) 1020s; δ_H 4.35 (6 H, m), 1.4–2.8 (3 H, m) and 1.38 (12 H, m); δ_F 34 (CF_2, m); *m/z* 303 (M + 1, 50.24%), 287 (M − CH_3, 5.78), 257 (M − OEt, 88) and 242 (M − OEt − CH_3, 100).

4-(*Diethoxyphosphoryl*)-4,4-*difluorobutyronitrile* **3g**. B.p. 114–116 °C/2 mmHg (Found: C, 39.2; H, 6.0; N, 5.7. $C_8H_{14}F_2NO_4P$ requires C, 39.83; H, 5.81; N, 5.81%); ν_{max}(neat)/cm^{-1} 2205w (CN), 1260s (P=O), 1160m (C–F) and 1020s; δ_H 4.37 (4 H, dq, $^4J_{HP}$ 10, $^3J_{HH}$ 7), 1.8–2.9 (4 H, m) and 1.42 (6 H, t, $^3J_{HH}$ 7); δ_F 36.0 (CF_2, dt, $^2J_{PF}$ 115, $^3J_{HF}$ 21); *m/z* 241 (M, 4.4%), 190 (100) and 137 (M − $CF_2CH_2CH_2CN$, 16).

Diethyl 1,1-*difluoro*-4-*oxopentylphosphonate* **3h**. B.p. 104–106 °C/2 mmHg (Found: C, 41.5; H, 6.7. $C_9H_{17}F_2O_4P$ requires C, 41.86; H, 6.59%); ν_{max}(neat)/cm^{-1} 1720s (C=O), 1280s (P=O), 1160m (C–F) and 1020s; δ_H 4.2 (4 H, dq, $^4J_{HP}$ 10, $^3J_{HH}$ 7), 2.18 (3 H, s), 1.6–2.8 (4 H, m) and 1.36 (6 H, t, $^3J_{HH}$ 7); δ_F 35 (CF_2), dt, $^2J_{PF}$ 115, $^3J_{HF}$ 21); *m/z* 259 (M + 1, 61%), 258 (M, 12) and 189 (M − $CH_2CH_2COCH_3$, 100).

Tetraethyl 1,1-*difluorotrimethylene*-1,3-*bisphosphonate* **3i** (Found: M^+, 325.0987. $C_{11}H_{24}F_2O_6P_2$ requires *M*, 325.1010); ν_{max}(neat)/cm^{-1} 1280 and 1240 (both s) (P=O), 1160s (C–F) and 1020s; δ_H 4.32 and 4.16 (8 H, 2 dq, $^4J_{HP}$ 10, $^3J_{HH}$ 7), 2.58 (4 H, m) and 1.38 and 1.26 (12 H, 2 t, $^3J_{HH}$ 7); δ_F 35 (CF_2, dt, $^2J_{PF}$ 116, $^3J_{HF}$ 21); *m/z* 353 (M + 1, 100%), 307 (M − OEt, 6.41), 215 [M − $PO(OEt)_2$, 25.16], 201 [M − $CH_2P(O)(OEt)_2$, 2.83], 187 [M − $CH_2CH_2P(O)(OEt)_2$, 7.06], 167 [M − $CF_2P(O)(OEt)_2$, 63.38] and 137 [$P(O)(OEt)_2$, 12.07].

Diethyl 1,1-*difluoro*-1-(3-*oxocyclohexyl*)*methylphosphonate* **3j** (Found: *m/z* 264.0962. $C_{11}H_{19}F_2O_4P$ − HF requires *m/z* 264.0921); ν_{max}(neat)/cm^{-1} 1720s (C=O), 1260s (P=O), 1160s (C–F) and 1020s; δ_H 4.26 (4 H, dq, $^4J_{HP}$ 10, $^3J_{HH}$ 7), 1.3–2.8 (9 H, m), 1.40 (6 H, t, $^3J_{HH}$ 7); δ_F 38 (CF_2, dd, $^2J_{PF}$ 115, $^3J_{HF}$ 18); *m/z* 285 (M + 1, 5.68%), 187 [$CF_2P(O)(OEt)_2$, 9.36), 147 [M − $P(O)(OEt)_2$, 4.97], 137 [$P(O)(OEt)_2$, 29.81], 127 [M − HF − $P(O)(OEt)_2$, 7.47] and 109 [PO(OH)(OEt), 100].

Tetraethyl 1,1,2,2-*tetrafluoroethylene*-1,2-*bisphosphonate* **5** (Found: M^+, 374.0680. $C_{10}H_{20}F_4O_6P_2$ requires *M*, 374.0666); ν_{max}(neat)/cm^{-1} 1280 and 1260 (both s) (P=O), 1160s (C–F) and 1080 and 1020 (both s); δ_H 4.26 (8 H, dq, $^4J_{HP}$ 10, $^3J_{HH}$ 7) and 1.36 (12 H, t, $^3J_{HH}$ 7); δ_F 42 (CF_2CF_2, d, $^2J_{PF}$ 115); *m/z* 375 (M + 1, 100%), 329 (M − OEt, 2.54), 187 [M − $CF_2P(O)(OEt)_2$, 0.74], 137 [$P(O)(OEt)_2$, 1.35] and 109 [PO(OH)(OEt), 6.34].

Diethyl 3-*chloro*-1,1-*difluoropropylphosphonate* **3k** (Found: *m/z*, 215.0619. $C_7H_{14}ClF_2O_3P$ − Cl requires *m/z* 215.0645); ν_{max}(neat)/cm^{-1} 1280s (P=O), 1160s (C–F), 1020s and 710w, (C–Cl); δ_H 4.32 (4 H, dq, $^4J_{HP}$ 10, $^3J_{HH}$ 7), 3.80 (2 H, t, $^3J_{HH}$ 8), 3.1–2.1 (2 H, m) and 1.38 (6 H, t, $^3J_{HH}$ 7); δ_F 34 (CF_2, dt, $^2J_{PF}$ 112, $^3J_{HF}$ 18); *m/z* 251 (M + 1, ^{35}Cl, 83.97%), 253 (M + 1, ^{37}Cl, 25.46), 215 (M − Cl, 10.61), 195 (M − Cl − HF, 8.09) and 109 [PO(OEt)(OH), 100].

Diethyl 1,1-*difluoropropylphosphonate* **6** (Found: M^+ 216.0762. $C_7H_{15}F_2O_3P$ requires *M*, 216.0723); ν_{max}(neat)/cm^{-1} 1380w (CH_2Me), 1280s (P=O), 1160m (C–F) and 1020s; δ_H 4.26 (4 H, q, $^4J_{HP}$ 10, $^3J_{HH}$ 7), 1.8–1.2 (2 H, m), 1.36 (6 H, t, $^3J_{HH}$ 7) and 1.10 (3 H, t, $^3J_{HH}$ 7); δ_F 33 (CF_2, dt, $^2J_{PF}$ 115, $^3J_{HF}$ 21); *m/z* 217 (M + 1, 100%), 197 (M − F, 2.82), 187 (M − CH_2CH_3, 0.96), 137 [$P(O)(OEt)_2$, 3.84], 109 [PO(OEt)(OH), 22.43] and 79 [M − $P(O)(OEt)_2$, 6.36].

Diethyl 3,3-*dichloro*-1,1-*difluoropropylphosphonate* **3l** Found: M^+, 283.9930. $C_7H_{13}Cl_2F_2O_3P$ requires *M*, 283.9945 (^{35}Cl × 2)]; ν_{max}(neat)/cm^{-1} 1280s (P=O), 1160s (C–F), 1020s and 730w (C–Cl); δ_H 6.05 (1 H, t, $^3J_{HH}$ 6.5 $CHCl_2$), 4.20 (4 H, dq, $^4J_{HP}$ 10, $^3J_{HH}$ 7), 3.4–2.5 (2 H, m) and 1.36 (6 H, t, $^3J_{HH}$ 7); δ_F 34 (CF_2, dt, $^2J_{PF}$ 108, $^3J_{HF}$ 20); *m/z* 285 [M + 1 (^{35}Cl × 2), 54.06%], 287 [M + 1 (^{35}Cl + ^{37}Cl), 41.45], 289 [M + 1 (^{37}Cl × 2), 7.06], 249 (M − Cl, 15.71), 137 [$P(O)(OEt)_2$, 30.87], 109 [PO(OEt)(OH), 100] and 77 (CF_2CH_2CH, 16.39).

Diethyl 3-*ethoxy*-1,1-*difluoropropylphosphonate* **3m**. B.p. 108–109 °C/5 mmHg (Found: C, 41.2; H, 7.4. $C_9H_{19}F_2O_4P$ requires C, 41.54; H, 7.31%); ν_{max}(neat)/cm^{-1} 1280s (P=O), 1120s (C=F) and 1020s; δ_H 4.5–3.8 (8 H, m), 2.8–2.0 (2 H, m) and 1.4 (9 H, m); δ_F 33 (CF_2, dt, $^2J_{PF}$ 115, $^3J_{HF}$ 21); *m/z* 261 (M + 1, 58%), 231 (M − Et, 95), 215 (M − OEt, 15), 137 [PO(OEt)(OH), 18] and 59 ($EtOCH_2$, 100).

Diethyl 1,1-*difluorobut*-3-*enylphosphonate* **3n**. B.p. 95–98 °C/1 mmHg (lit., 60–62 °C/0.05 mmHg); ν_{max}(neat)/cm^{-1} 1645w (C=C), 1280s, (P=O), 1160m (C–F) and 1020s; δ_H 4.9–6.1 (3 H, m, $CH=CH_2$), 4.15 (4 H, dq, $^4J_{HP}$ 10, $^3J_{HH}$ 7), 2.6 (2 H, tt, $^3J_{HF}$ 21, $^3J_{HH}$ 7 and 1.30 (6 H, t, $^3J_{HH}$ 7); δ_F 33 (CF_2, dt, $^2J_{PF}$ 115, $^3J_{HF}$ 21); *m/z* 229 (M + 1, 100%).

Acknowledgements

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