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REACTION OF F-ALKANOIC ACID CHLORIDES WITH TRIALKYL PHOSPHITES LEADING TO 1-(DIALKOXYPHOSPHINYL)OXY-F-1-ALKENEPHOSPHONATES OR 1-(DIALKOXYPHOSPHINYL)OXY-1H-F-ALKANEPHOSPHONATES*

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SUMMARY

F-Alkanoic acid chlorides exothermically reacted with 2 equivalents of trialkyl phosphite without solvent at -20 °C to ambient temperature to give the corresponding dialkyl (Z)-1-(dialkoxyphosphinyl)oxy-F-1-alkenephosphonate in high yields. When the reaction was conducted at -78 °C in an ethereal solvent, dialkyl 1-(dialkoxyphosphinyl)oxy-1H-F-alkanephosphonate was obtained exclusively in place of the former alkenephosphonate. No F-acylphosphonate was detected in spite of the amount of the phosphite, the mode of addition, and the reaction temperature being varied.

INTRODUCTION

The reaction of alkyl halides with trialkyl phosphite (Michaelis-Arbuzov reaction) is an important method widely used for the synthesis of a variety of phosphorus-containing compounds [1]. The products of the Michaelis-Arbuzov or

$$RCCl + P(OR^1)_3 \longrightarrow RC(=O)-P(=O)(OR^1)_2 + R^1Cl$$

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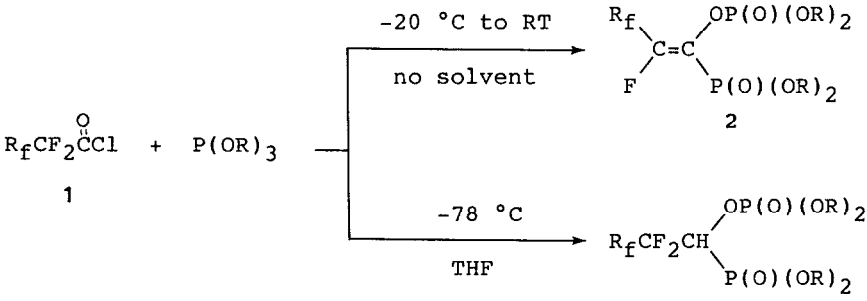
Baeker type reaction of acyl halides with trialkyl [2] or dialkyl phosphite [3] are the corresponding acylphosphonates, whose synthetic utility has recently been demonstrated in many organic transformations [2d,4]. F-Alkanoic acid chlorides are known to react with dialkyl phosphite in the presence of a tertiary amine such as triethylamine to afford F-acylphosphonates [5], which can be used as a perfluoroacylating agent for alcohols and amines [5b].

In connection with our recent studies on the reactions and synthetic applications of fluorinated carbonyl compounds and their derivatives [6], we have examined the reaction of F-alkanoic acid chlorides (**1**) with trialkyl phosphites and have found that this reaction proceeds smoothly to result in the selective formation of dialkyl (Z)-1-(dialkoxyphosphinyl)oxy-F-1-alkenephosphonates (**2**) or 1-(dialkoxyphosphinyl)oxy-1H-F-alkanephosphonates (**3**), depending on the reaction conditions, particularly on the reaction temperature (Scheme 1).



Scheme 1

The recent report by Brittelli [7] on the reaction of 2-haloacyl halides with trialkyl phosphites prompted us to disclose our independent results of the related reaction of F-alkanoic acid chlorides. This paper describes several characteristics of such reaction as well as its possible reaction mechanism.

RESULTS AND DISCUSSION

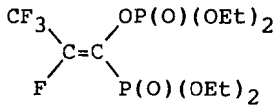
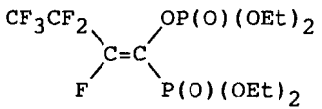
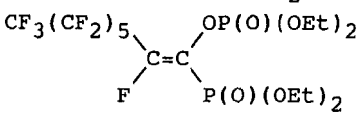
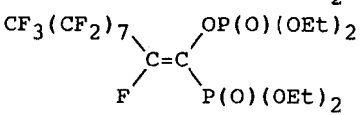
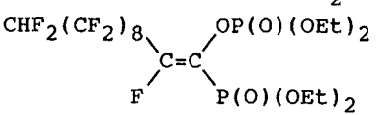
F-Alkanoic acid chlorides employed in the present study are F-propanoyl (**1a**), F-butanoyl (**1b**), F-octanoyl (**1c**), F-

decanoyl (**1d**), and 11H-F-undecanoyl chlorides (**1e**), which were easily prepared in 70-90% yields by the reaction between the corresponding sodium salt of an acid and an appropriate chlorinating agent [8]. When acid chloride **1b** was added to an equimolar amount of triethyl phosphite in the absence of a solvent under cooling (-40 to -20 °C), followed by warmup to room temperature and stirring for 2 h, the product **2b** was exclusively formed and a half amount of **1b** remained unchanged. The corresponding F-acylphosphonate (**4b**) could not be detected in the reaction mixture. Even by changing either of the mode of addition or of the ratio of phosphite to **1b**, no **4b** could be produced. The reaction of **1b** with two equivalents of the phosphite proceeded cleanly to give a high yield of **2b**, the starting acid chloride being completely consumed. Other acid chlorides, **1a**, **1c**, **1d**, and **1e**, underwent the reaction with triethyl phosphite under similar conditions to afford the corresponding alkenephosphonates (**2**) in good yields. The stereochemistry of **2** was determined on the basis of the magnitudes of the coupling between a vinylic fluorine and a phosphorus atom in a phosphonate or phosphate group. Table 1 summarizes the results of this type of reaction.

To be noted is that in all cases the hydrolytic workup of the reaction mixture occurred exothermically. This observation is strongly suggestive of the formation of a certain intermediate which is capable of leading to the product **2** by hydrolysis. ^{19}F and ^{31}P NMR analyses in the reaction of **1b** with triethyl phosphite were done before quenching with water: In the ^{19}F NMR spectra of the reaction mixture, three kinds of peaks appeared upfield from trifluoroacetic acid as an external standard. These are a doublet with a coupling constant of 4.9 Hz centered at -6.75 ppm, a broad doublet with a coupling constant of 5.6 Hz centered at -40.0 ppm, and a broad multiplet centered at -72.5 ppm, to which the trifluoromethyl, difluoromethylene, and fluoromethine (vinylic) groups can be assigned, respectively. ^{31}P NMR spectra exhibited two sets of a doublet located at -6.73 and -70.5 ppm upfield from external phosphoric acid. The former has a coupling constant of 9.8 Hz, to which a phosphinyl moiety can be assigned, and the latter broad doublet has a coupling constant of 809.2 Hz, to

TABLE 1

Preparation of diethyl (Z)-1-(diethoxyphosphinyl)oxy-F-1-alkenephosphonates (2)

Product 2	Yield %	Bp[a] of 2 °C/mmHg		^{31}P NMR[b] δ
	(2a)	77	90/2.0	2.82, -6.32
	(2b)	79	100/2.0	2.72, -6.53
	(2c)	67	-	2.88, -6.49
	(2d)	66	-	2.80, -6.64
	(2e)	69	-	2.70, -6.68

[a] Oven temperature on Kugelrohr distillation.

[b] The downfield shifts from the reference are expressed positive.

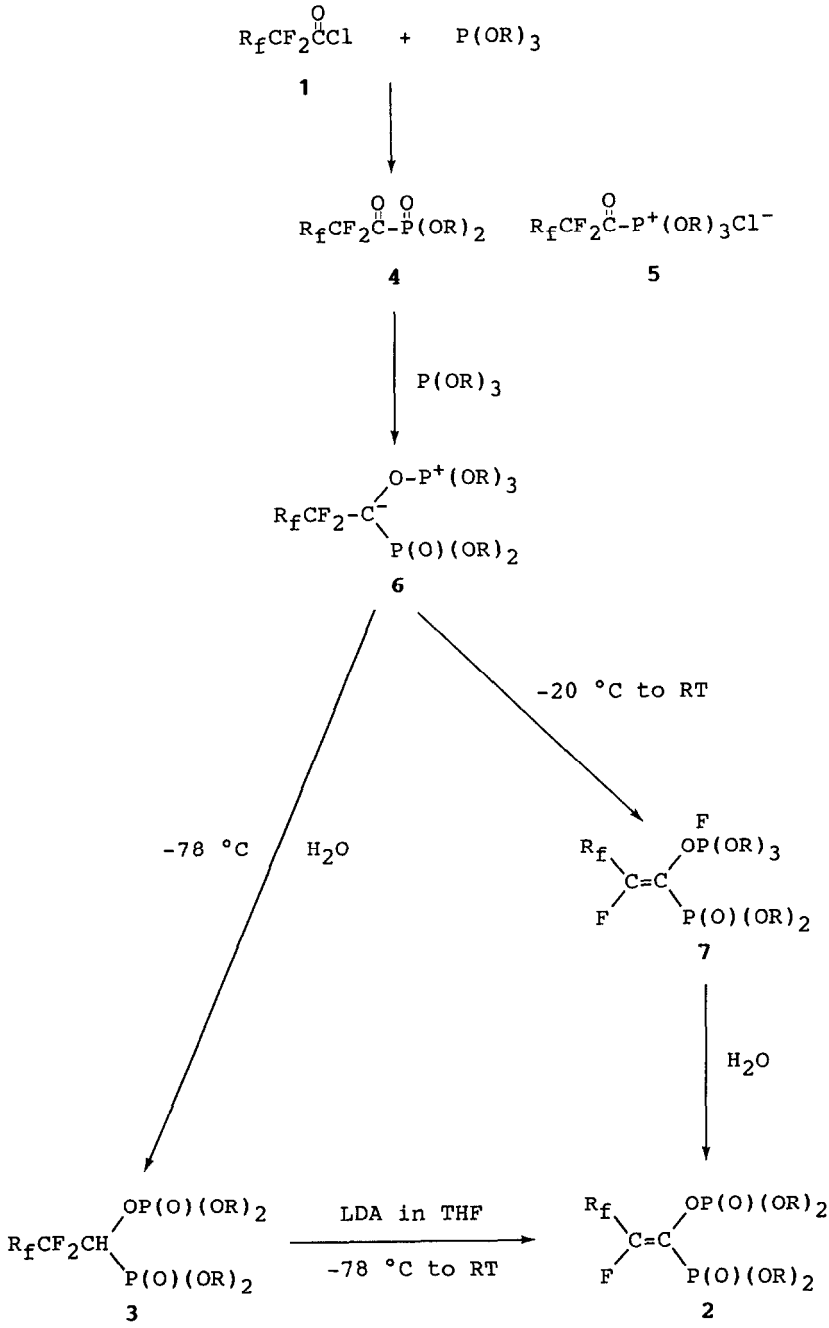
which a phosphorus nucleus in a phosphorane structure can be assigned. These spectroscopic data and the above-cited observation allow us to deduce the structure **7** depicted in Scheme 2 as a possible intermediate.

When the reaction was carried out at -78 °C by using a 2:1 molar ratio of trialkyl phosphite to **1** and was quenched with water-methanol at the same temperature, dialkyl 1-(dialkoxyphosphinyl)oxy-1H-F-alkanephosphonates (**3**) were obtained, instead of **2**, in good yields as listed in Table 2.

TABLE 2
Preparation of dialkyl 1-(dialkoxyphosphinyl)oxy-1H-F-alkanephosphonates (**3**)

Product **3**		Yield of **3** %
$CF_3CF_2CH(OP(O)(OEt)_2)P(O)(OEt)_2$	(**3a**)	68
$CF_3CF_2CF_2CH(OP(O)(OEt)_2)P(O)(OEt)_2$	(**3b**)	74
$CF_3CF_2CF_2CH(OP(O)(OMe)_2)P(O)(OMe)_2$	(**3c**)	70

Quenching of the reaction, which had been performed at -78 °C followed by warmup to room temperature, led to a predominant formation of alkenephosphonate **2b**. Of much significance is that the treatment of acid chloride **1b** with triethyl phosphite in the presence of diethyl phosphite as a proton source afforded **3b** together with a trace amount of **2b**, in spite of the reaction temperature being -20 °C to room temperature. These findings make it reasonable to assume that transient species **6** is formed in the present reaction; the elimination of β-fluorine atom in **6** occurs easily to give the before-mentioned intermediate (**7**) at a higher temperature (-20


$R_fCF_2\overset{O}{\overset{\|}{C}}Cl$ + $P(OR)_3$
1
$R_fCF_2\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{P}}(OR)_2$
4
$R_fCF_2\overset{O}{\overset{\|}{C}}-P^+(OR)_3Cl^-$
5
$P(OR)_3$
$R_fCF_2-C^-(O-P^+(OR)_3)(P(O)(OR)_2)$
6
-20 °C to RT
-78 °C
H_2O
$R_f(F)C=C(OP(OR)_3)(P(O)(OR)_2)$
7
H_2O
$R_fCF_2CH(OP(O)(OR)_2)(P(O)(OR)_2)$
3
LDA in THF
-78 °C to RT
$R_f(F)C=C(OP(O)(OR)_2)(P(O)(OR)_2)$
2

Scheme 2

°C to room temperature), whereas at a lower temperature (-78 °C) the intermediate **6** is converted to the product **3** by protonolysis with water or dialkyl phosphite. Moreover, the success in converting **3** into **2** by use of lithium diisopropylamide (see Experimental section) provides a further support for the intermediacy of **6**, because such a reaction proceeds through a carbanionic intermediate similar to **6**.

As described earlier, alkenephosphonates **2** are exclusively formed irrespective of the amount of the phosphite used, and two molar equivalents of the phosphite is needed for completion of the reaction. These features can be explained by assuming that trialkyl phosphite reacts with **1** to give as the initial adduct F-acylphosphonate **4**, which reacts much more rapidly than acid chloride **1** with a second phosphite to afford **6**. This assumption is based on the fact [5b] that F-acylphosphonate readily reacts with dialkyl phosphite to give the corresponding **3**. No evidence, however, for the existence of intermediate 4 has been obtained in our hand at present*. The possibility cannot be ruled out that F-acylphosphonium salt (**5**) might be an intermediate in place of **4**, as proposed by Brittelli [7].

In summary, the present reaction of **1** with trialkyl phosphite takes place easily to give (Z)-1-(dialkoxyphosphinyl)-oxy-F-1-alkenephosphonates (**2**) or 1-(dialkoxyphosphinyl)oxy-1H-F-alkanephosphonates (**3**) in good yields, selectivity in their formation being dependent on the reaction temperature. These new compounds obtained here can serve as a good precursor for preparing a variety of organic fluorine compounds; some synthetic applications of these compounds have been reported in our recent papers [9].

EXPERIMENTAL

Infrared spectra (IR) were recorded on a Shimadzu IR-400 infrared spectrometer by using a polystyrene film for cali-

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*All attempts were unsuccessful to prepare compound **4** by the reported method [5a]. The use of a phosphite with a readily removable substituent such as diethyl trimethylsilyl phosphite was also not effective for synthesizing **4**.

bration. ^{1}H and ^{19}F NMR spectra were obtained with a Varian EM-390 spectrometer in solutions of carbon tetrachloride (CCl_4) or chloroform-d ($CDCl_3$). A JEOL FX-90Q computer-controlled spectrometer was used to measure ^{19}F and ^{31}P NMR spectra for solutions in $CDCl_3$ with trifluoroacetic acid (TFA) and 85% phosphoric acid (H_3PO_4) as an external reference, respectively. The proton, fluorine, and phosphorus chemical shifts are reported in parts per million (ppm) downfield from Me_4Si, TFA, and H_3PO_4, respectively. Mass spectra (MS) were taken on a Hitachi RMS-4 mass spectrometer operating at an ionization potential of 70 eV.

All chemicals were of reagent grade and, if neccessary, were distilled or vacuum-distilled prior to use. Solvents were purified in the conventional manner.

F-Alkanoic acid chlorides (**1**) were prepared according to the literature methods [8].

Reaction of F-alkanoic acid chlorides **1** with triethyl phosphite giving diethyl (Z)-1-(diethoxyphosphinyl)oxy-F-1-alkenephosphonates **2**

In a three-necked round-bottomed flask, equipped with a teflon stirrer, a thermometer, a rubber septum, and an inlet tube for nitrogen, was placed 200 mmol of triethyl phosphite which had been distilled over sodium metal. After the flask was cooled by immersing in an ice-salt or dry ice-methanol bath, 100 mmol of freshly prepared F-alkanoic acid chloride **1** was introduced to it via a syringe at such a rate that the reaction temperature was maintained below 30 °C. The whole mixture was stirred at room temperature for 2 h. To this mixture, re-cooled to 0°C, was gradually added 30-50 ml of water by use of a syringe. The resultant solution was subjected to extraction with ether (50 ml x 3) and the ethereal extracts were washed with 5% aqueous sodium hydrogen carbonate, dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The residue was distilled or chromatographed on silica gel to give pure product **2** as a viscous oil.

Diethyl (Z)-1-(diethoxyphosphinyl)oxy-F-1-propenephosphonate (2a) (nc)

77% yield; Bp 90 °C (2 mmHg); IR (film) 2980 (s), 2940 (m), 1655 (w), 1485 (m), 1445 (m), 1395 (m), 1365 (s), 1280 (s), 1215 (s), 1150 (s), 1100 (s), 1020 (s), 980 (s), 860 (s), 810 (m), 755 (m) cm^{-1}; ^{1}H NMR (CCl_4) δ 1.37 (t, J = 7.2 Hz, 12H) and 4.20 (dq, J = 7.2 and 7.2 Hz, 8H); ^{19}F NMR (CCl_4, TFA) δ 10.5 (d, J = 8.5 Hz, 3F) and -61.8 (br q, J = 8.5 Hz, 1F); ^{31}P NMR ($CDCl_3$, H_3PO_4) δ 2.82 (dd, J = 10.7 and 3.1 Hz, 1P) and -6.32 (ddq, J = 10.7, 3.0, and 2.0 Hz, 1P); MS (m/e) 402 (M^+). Anal. Calcd for $C_{11}H_{20}F_4O_7P_2$: C, 32.84; H, 4.98; F, 18.91 %. Found: C, 32.65; H, 5.12; F, 18.67 %.

Diethyl (Z)-1-(diethoxyphosphinyl)oxy-F-1-butenephosphonate (2b) (nc)

79% yield; Bp 100 °C (2 mmHg); IR (film) 2950 (m), 2930 (m), 1770 (w), 1490 (m), 1455 (m), 1405 (m), 1380 (m), 1345 (m), 1285 (s), 1230 (s), 1195 (s), 1155 (s), 1030 (s), 990 (s), 870 (s), 810 (s), 760 (s), 730 (m) cm^{-1}; ^{1}H NMR (CCl_4) δ 1.38 (t, J = 6.0 Hz, 12H) and 4.22 (dq, J = 6.0 and 6.0 Hz, 8H); ^{19}F NMR (CCl_4, TFA) δ -5.50 (dt, J = 7.1 and 2.8 Hz, 3F), -41.0 (br d, J = 9.9 Hz, 2F), and -59.8 (ddtq, J = 9.9, 7.1, 3.0, and 3.0 Hz, 1F); ^{31}P NMR ($CDCl_3$, H_3PO_4) δ 2.72 (br d, J = 9.2 Hz, 1P) and -6.53 (ddt, J = 9.2, 3.0, and 2.7 Hz, 1P); MS (m/e) 452 (M^+). Anal. Calcd for $C_{12}H_{20}F_6O_7P_2$: C, 31.86; H, 4.43; F, 25.22 %. Found: C, 32.13; H, 4.54; F, 24.96 %.

Diethyl (Z)-1-(diethoxyphosphinyl)oxy-F-1-octenephosphonate (2c) (nc)

67% yield; IR (film) 2980 (s), 2940 (m), 2910 (m), 1780 (w), 1480 (m), 1445 (m), 1395 (m), 1370 (m), 1280 (s), 1240 (s), 1200 (vs), 1150 (s), 1100 (s), 1010 (vs), 985 (s), 860 (s), 810 (m), 730 (m), 710 (m) cm^{-1}; ^{1}H NMR (CCl_4) δ 1.37 (t, J = 7.5 Hz, 12H) and 4.20 (dq, J = 7.5 and 7.5 Hz, 8H); ^{19}F NMR (CCl_4, TFA) δ -2.90 (s, 3F), -37.4 (dt, J = 11.2 and 11.2 Hz, 2F), -42.8 to -45.3 (m, 6F), -47.1 to -53.4 (m, 2F), and -59.1 (m, 1F); ^{31}P NMR ($CDCl_3$, H_3PO_4) δ 2.88 (br d, J = 9.5 Hz, 1P) and -6.49 (ddt, J = 9.5, 2.7, and 2.7 Hz, 1P). Anal. Calcd for $C_{16}H_{20}F_{14}O_7P_2$: C, 29.45; H, 3.07; F, 40.80 %. Found: C, 29.70; H, 3.16; F, 40.61 %.

Diethyl (Z)-1-(diethoxyphosphinyl)oxy-F-1-decenephosphonate (**2d**) (nc)

66% yield; IR (film) 2990 (m), 2940 (m), 1780 (m), 1480 (w), 1445 (m), 1395 (m), 1370 (m), 1275 (s), 1240 (s), 1210 (vs), 1150 (s), 1030 (s), 985 (s), 865 (m), 800 (m), 760 (m), 720 (m), 705 (m) cm^{-1}; ^{1}H NMR (CCl_4) δ 1.37 (t, J = 7.5 Hz, 12H) and 4.22 (dq, J = 7.5 and 7.5 Hz, 8H); ^{19}F NMR (CCl_4, TFA) δ -2.80 (t, J = 8.5 Hz, 3F), -37.8 (m, 2F), -43.0 to -45.3 (m, 10F), -47.8 (m, 2F), and -57.7 (m, 1F); ^{31}P NMR ($CDCl_3$, H_3PO_4) δ 2.80 (br d, J = 9.1 Hz, 1P) and -6.64 (dd, J = 9.1 and 2.5 Hz, 1P). Anal. Calcd for $C_{18}H_{20}F_{18}O_7P_2$: C, 28.72; H, 2.66; F, 45.48 %. Found: C, 28.63; H, 2.72; F, 45.17 %.

Diethyl (Z)-1-(diethoxyphosphinyl)oxy-11H-F-1-undecenephosphonate (**2e**) (nc)

69% yield; IR (film) 2980 (m), 1800 (w), 1440 (w), 1394 (w), 1370 (w), 1270 (s), 1210 (vs), 1143 (s), 1020 (vs), 978 (m), 855 (m), 794 (m), 728 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.37 (t, J = 6.0 Hz, 12H) and 4.27 (dq, J = 6.0 and 6.0 Hz, 8H); ^{19}F NMR ($CDCl_3$, TFA) δ -37.8 (br s, 2F), -43.8 (br s, 10F), -45.3 (br s, 2F), -51.3 (br s, 2F), -58.3 (m, 1F), and -59.4 (br d, J = 52.2 Hz, 2F); ^{31}P NMR ($CDCl_3$, H_3PO_4) δ 2.70 (d, J = 8.9 Hz, 1P) and -6.68 (d, J = 8.9 Hz, 1P). Anal. Calcd for $C_{19}H_{21}F_{19}O_7P_2$: C, 29.08; H, 2.68; F, 46.05 %. Found: C, 29.37; H, 2.87; F, 45.83 %.

Reaction of F-alkanoic acid chlorides **1** with trialkyl phosphite at -78 °C affording dialkyl 1-(dialkoxyphosphinyl)oxy-1H-F-alkanephosphonates **3**

To a solution of 20 mmol of trialkyl phosphite in tetrahydrofuran (THF) was dropwise added 10 mmol of F-alkanoic acid chloride **1** at -78 °C under a nitrogen atmosphere. This mixture was stirred for 2 h at -78 °C and thereafter the reaction was quenched with water-methanol at the same temperature. The resulting mixture was extracted with ether (30 ml x 3). The ethereal extracts were washed with 5% aqueous sodium hydrogen carbonate and with water, followed by drying over

anhydrous sodium sulfate, filtration, and concentration *in vacuo*. Column chromatography of the residual oil on silica gel gave analytically pure product **3**.

Diethyl 1-(diethoxyphosphinyl)oxy-1H-F-propanephosphonate (**3a**) (nc)

68% yield; IR (film) 2980 (s), 2910 (m), 1480 (m), 1445 (m), 1395 (m), 1370 (m), 1280 (vs), 1195 (vs), 1145 (vs), 1100 (s), 1020 (vs), 980 (vs), 860 (s), 810 (m), 750 (m), 720 (m) cm^{-1}; ^1H NMR (CCl_4) δ 1.33 (ddt, *J* = 1.4, 1.4, and 7.1 Hz, 6H), 1.38 (t, *J* = 7.1 Hz, 6H), 3.8-4.3 (m, 8H), and 4.6-5.2 (m, 1H); ^{19}F NMR (CCl_4, TFA) δ -3.5 (s, 3F), -38.8 (ddd, *J* = 279, 11.2, and 5.6 Hz, 1F), and -43.7 (ddd, *J* = 279, 16.9, and 5.6 Hz, 1F); MS (*m/e*) 422 (M^+). Anal. Calcd for $C_{11}H_{21}F_5O_7P_2$: C, 31.28; H, 4.98; F, 22.51 %. Found: C, 31.09; H, 4.90; F, 22.34 %.

Diethyl 1-(diethoxyphosphinyl)oxy-1H-F-butanephosphonate (**3b**)

74% yield; IR (film) 2980 (m), 2920 (m), 2910 (m), 1475 (m), 1440 (m), 1390 (m), 1365 (m), 1345 (m), 1270 (vs), 1220 (vs), 1185 (vs), 1160 (s), 1130 (s), 1105 (vs), 1030 (vs), 975 (vs), 920 (m), 860 (s), 800 (m), 725 (m) cm^{-1}; ^1H NMR (CCl_4) δ 1.34 (dt, *J* = 6.9 and 1.5 Hz, 6H), 1.38 (t, *J* = 6.9 Hz, 6H), 3.9-4.4 (m, 8H), and 4.8-5.4 (m, 1H); ^{19}F NMR (CCl_4, TFA) δ -2.7 (dd, *J* = 11.3 and 11.3 Hz, 3F), -36.1 (br d, *J* = 296 Hz, 1F), -40.6 (br d, *J* = 296 Hz, 1F), and -47.1 (m, 2F); MS (*m/e*) 472 (M^+).

Dimethyl 1-(dimethoxyphosphinyl)oxy-1H-F-butanephosphonate (**3c**)

70% yield; IR (film) 2960 (m), 2920 (m), 2860 (m), 1450 (m), 1350 (m), 1280 (vs), 1230 (vs), 1185 (vs), 1135 (s), 1110 (vs), 1040 (vs), 980 (m), 960 (m), 925 (m), 870 (s), 850 (s), 810 (w), 785 (m), 755 (m), 735 (m), 705 (w) cm^{-1}; ^1H NMR (CCl_4) δ 3.74 (dd, *J* = 8.0 and 12.1 Hz, 6H), 3.83 (dd, *J* = 1.5 and 11.0 Hz, 6H), and 4.8-5.4 (m, 1H); ^{19}F NMR (CCl_4, TFA) δ -2.5 (dd, *J* = 9.9 and 11.3 Hz, 3F), -36.4 (br d, *J* = 288 Hz, 1F), -40.8 (br d, *J* = 288 Hz, 1F), and -47.2 (m, 2F); MS (*m/e*) 416 (M^+).

Treatment of diethyl 1-(diethoxyphosphinyl)oxy-1H-F-butane-phosphonate **3b** with lithium diisopropylamide

To a mixture of 6 mmol of lithium diisopropylamide, prepared from diisopropylamine and butyllithium in THF, was added a solution of 5 mmol of **3b** in THF at -78 °C under nitrogen. After being stirred for 2 h at the same temperature followed by warmup to room temperature, the mixture was treated with a saturated aqueous solution of ammonium chloride. The resultant solution was subjected to extraction with ether (15 ml x 3). The extracts were washed with water, dried over anhydrous sodium sulfate, filtered, and concentrated under vacuum. The residual oil was chromatographed on silica gel with ether to give diethyl (Z)-1-(diethoxyphosphinyl)oxy-F-1-butenephosphonate **2b** in 71% yield.

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