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SELECTIVE PREPARATION OF 1-SUBSTITUTED 2,2-DIFLUOROETHENYL PHOSPHATES OR 1-HYDROXYALKANEPHOSPHONATES THROUGH THE REACTION OF CHLORODIFLUOROMETHYL KETONES WITH DIALKYL OR DIARYL PHOSPHITES

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SUMMARY

Various chlorodifluoromethyl ketones react readily with dialkyl or diaryl phosphites in the presence of triethylamine at the reflux temperature of tetrahydrofuran to give the corresponding dialkyl or diaryl 1-substituted-2,2-difluoroethenyl phosphates in good yields, whereas the similar reaction conducted at lower temperature (0-20 °C) affords 1-(chlorodifluoromethyl)-1-hydroxyalkanephosphonates almost exclusively. The latter compounds are converted to the former enol phosphates by the treatment with triethylamine or sodium methoxide in refluxing tetrahydrofuran.

INTRODUCTION

The reactions of alkyl halides with trialkyl or dialkyl phosphites are well known as the Michaelis-Arbuzov or Michaelis-Becker reaction, respectively. These reactions are frequently used for the synthesis of a variety of phosphorus-containing compounds. α-Halo ketones also undergo such a reaction with phosphites to give β-keto phosphonates (Arbuzov-type products), enol phosphates (Perkow-type products), and/or 1,2-epoxyphosphonates [1-6]. Preference in their formation is strongly dependent on the nature of the starting α-halo

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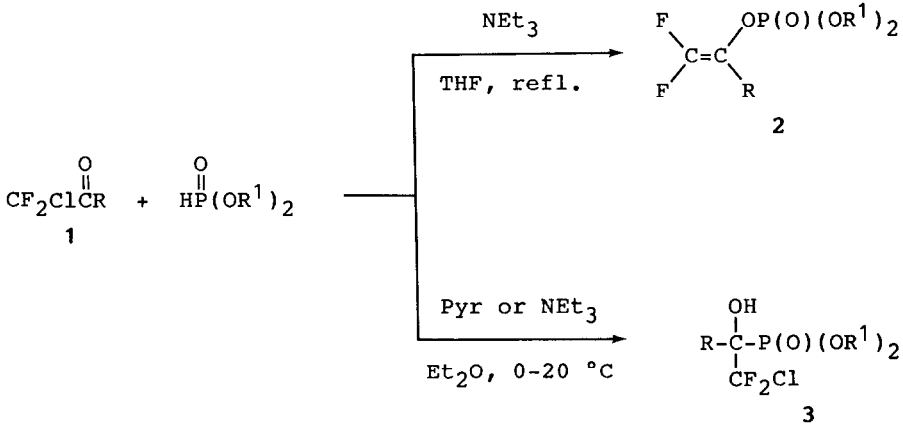
ketones and the reaction conditions employed [1-6]. The recent works [6] on the preparation and reactions of silylated phosphites have made the mechanism of the Perkow reaction clear. In the literature, however, there are only scattered reports on the reaction between fluorinated ketones and dialkyl or trialkyl phosphites [7].

As a part of our studies [8] to extend synthetic utility of fluorine-containing carbonyl compounds and their derivatives, we reported very recently that F-alkanoyl chlorides reacted with triethyl phosphite to give 1-[(diethoxyphosphinyl)oxy]-F-1-alkenephosphonates [9], which were employed as good precursors for the synthesis of various F-1-alkenoic acid derivatives [10].



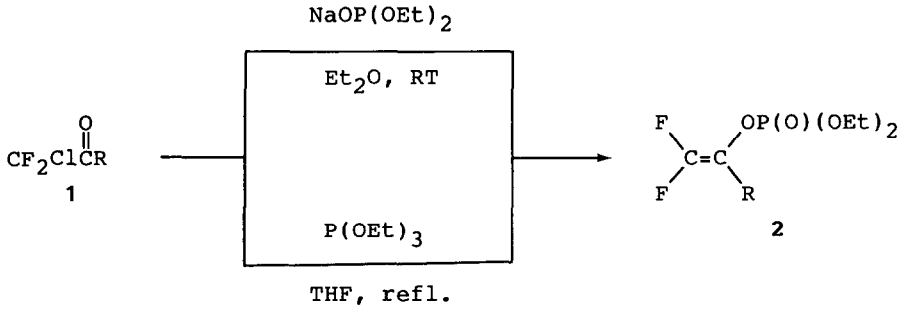
Scheme 1

In this paper, we wish to describe our results of the reaction between chlorodifluoromethyl ketones (**1**) and dialkyl or diaryl phosphites (Scheme 1). The findings reported herein will become additional evidence elucidating successfully the Perkow reaction of α-halo ketones.

RESULTS AND DISCUSSION

The starting chlorodifluoromethyl ketones (**1**) were available from chlorodifluoroacetic acid and Grignard reagents according to the literature method [11]. A ketone 1 thus

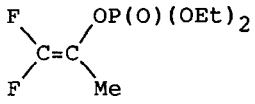
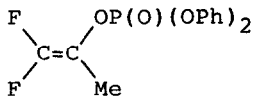
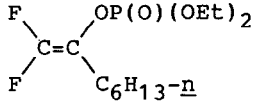
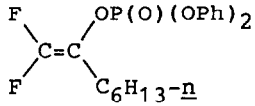
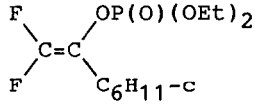
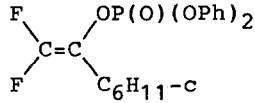
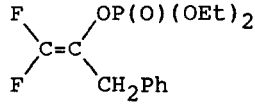
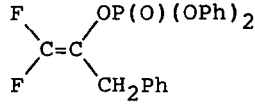
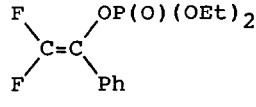
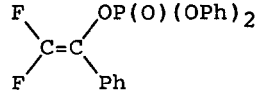
obtained was treated with a dialkyl or diaryl phosphite in the presence of a base at the reflux temperature of tetrahydrofuran (THF) to give good yields of the corresponding dialkyl or diaryl 1-substituted-2,2-difluoroethenyl phosphate (**2**) (Scheme 1). The results are summarized in Table 1. This reaction was facilitated by the presence of a tertiary amine such as triethylamine or pyridine, which acts as a base for equilibrating a pentavalent species of the phosphite to a more nucleophilic trivalent species as well as for trapping hydrogen chloride liberated during the reaction. The reaction without the amine took place sluggishly or gave a mixture of enol phosphate **2** and 1-hydroxyalkanephosphonate **3**. Noteworthy in this connection is that the anion generated from a dialkyl phosphite and sodium hydride smoothly reacted with **1** at room temperature to afford the enol phosphate **2** in a comparable yield. Furthermore, triethyl phosphite was also found to react with a ketone **1** at the reflux temperature of THF to give rise to a diethyl 1-substituted-2,2-difluoroethenyl phosphate (**2**) in good yield, as shown in Scheme 2. None of the β-keto phosphonates (Arbuzov-type products) were detected in these reactions.



Scheme 2

When the reaction of a ketone **1** with a dialkyl phosphite was performed at 0-20 °C, a 1-(chlorodifluoromethyl)-1-hydroxyalkanephosphonate (**3**) was produced preferentially. Table 2 summarizes the yields of the products, together with some reaction conditions. Either triethylamine or pyridine was effective, though the use of the less basic pyridine necessi-

TABLE 1
Syntheis of 1-substituted 2,2-difluoroethenyl phosphates (2) from chlorodifluoromethyl ketones (1)

Entry	Ketone R	Phosphite R^1	Time h	Product 2		Yield[a] %
1	Me	Et	96		(2a)	89[b]
2	Me	Ph	24		(2b)	80
3	$\underline{n}$-C_6H_{13}	Et	72		(2c)	65
4	$\underline{n}$-C_6H_{13}	Ph	72		(2d)	64
5	c-C_6H_{11}	Et	24		(2e)	90[b]
6	c-C_6H_{11}	Ph	24		(2f)	77
7	$PhCH_2$	Et	48		(2g)	73
8	$PhCH_2$	Ph	24		(2h)	62
9	Ph	Et	24		(2i)	79
10	Ph	Ph	24		(2j)	73

[a] Isolated yields. [b] Determined by ^{19}F NMR.

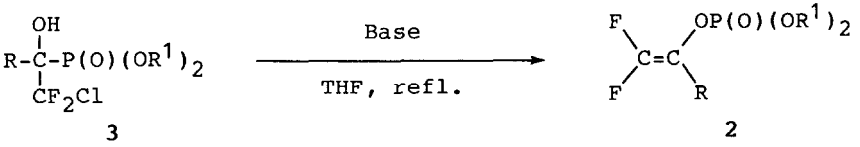
TABLE 2

Synthesis of 1-(chlorodifluoromethyl)-1-hydroxyalkanephosphonates (**3**) from chlorodifluoromethyl ketones (**1**) and diethyl phosphite

Entry	Ketone **1**	Amine	Temp °C	Time h	Yield[a] (%) of **2**	Yield[a] (%) of **3**
1	$CF_2ClC(=O)Me$	NEt_3	0	5	5	95
2	$CF_2ClC(=O)C_6H_{13}$-n	NEt_3	0	24	3	96
3	$CF_2ClC(=O)C_6H_{11}$-c	NEt_3	0	8	25	55
4	$CF_2ClC(=O)CH_2Ph$	Pyridine	20	96	0	88
5		NEt_3	20	3	25	75
6		NEt_3	5	5	18	59
7		NEt_3	5	1	4	95
8	$CF_2ClC(=O)Ph$	Pyridine	20	128	22	74
9		NEt_3	0	5	72	27

[a] Determined by ^{19}F NMR.

tated a much longer reaction time than for triethylamine (entries 4 and 8 in Table 2). It should be noted that a lower reaction temperature than room temperature and an equimolar amount of amine are crucial for the selective formation of **3**, since nonfluorinated 2-halo-1-hydroxyalkanephosphonates are usually prepared by the thermal or base-catalyzed reaction of α-halo carbonyl compounds with dialkyl phosphites [12].



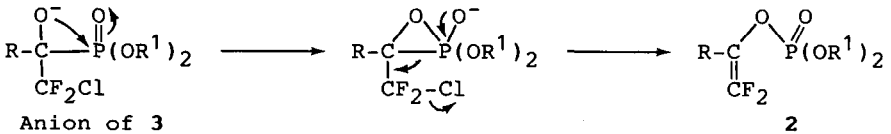
3 **2**

Scheme 3

A phosphonate **3** was readily converted into the corresponding enol phosphate **2** quantitatively on treatment with a base such as triethylamine or sodium methoxide (Scheme 3). This fact strongly suggests that **3** is an intermediate in the amine-promoted reaction between **1** and dialkyl or diaryl phosphite leading to **2**. Moreover, the fact is in sharp contrast to that observed for the reaction of fluorine-free 2-halo-1-hydroxyalkanephosphonates with a base, where 1,2-epoxyphosphonates and/or β-keto phosphonates are formed [12]. It is apparent that the presence of fluorine atoms on the carbon carrying a chlorine substituent is responsible for inhibiting the formation of 1,2-epoxy- or β-keto phosphonates in the present reaction.

The above-noted Michaelis-Becker-type reaction of **1** can be explained by a mechanism similar to that proposed previously for the reaction of α-halo carbonyl compounds with phosphites [6,13]. Thus, a nucleophilic trivalent species of dialkyl or diaryl phosphite attacks the carbonyl carbon atom of **1** to produce 1-hydroxyalkanephosphonate **3**. The phosphoryl group of **3** undergoes intramolecular attack by the relatively acidic hydroxyl function, which probably exists to a limited extent as its oxyanion in an alkaline medium. Simultaneous cleavage of a carbon-phosphorus and carbon-chlorine bond via a

phosphorus-containing three-membered ring transition state, or intermediate, affords 2,2-difluoroethenyl phosphate **2**.



Anion of **3** **2**

Scheme 4

The fluorinated organophosphorus compounds prepared in this study have been shown to serve as useful intermediates for the synthesis of 1,1-difluoroolefins [8d] and α,α-difluoro-β-hydroxy ketones [14]. Several compounds of types **2** and **3** have exhibited certain herbicidal and/or insecticidal activities [14].

EXPERIMENTAL

Infrared spectra (IR) were taken on a Shimadzu IR-400 infrared spectrometer by using a polystyrene film for calibration. ^{1}H and ^{19}F NMR spectra were recorded with a Varian EM-390 spectrometer in solutions of carbon tetrachloride (CCl_4). A JEOL FX-90Q computer-controlled spectrometer was used to measure ^{19}F NMR spectra for solutions in chloroform-d ($CDCl_3$) with trifluoroacetic acid (TFA) as an external standard. The proton and fluorine chemical shifts are given in parts per million (ppm) downfield from tetramethylsilane and TFA, respectively. Mass spectra (MS) were obtained with a Hitachi RMS-4 mass spectrometer operating at an ionization potential of 70 eV.

Commercially available chlorodifluoroacetic acid was used without any purification. Diethyl or diphenyl phosphite was vacuum-distilled over calcium hydride, and triethyl phosphite was purified by distillation over sodium metal prior to use. All solvents and other chemicals employed in this study were of reagent grade and were purified in the conventional manner.

The starting chlorodifluoromethyl ketones **1** were obtained by the reaction of chlorodifluoroacetic acid with Grignard reagents [11].

Reaction of ketone 1 with dialkyl phosphite at the reflux temperature of THF leading to enol phosphate 2

In a three-necked round-bottomed flask, fitted with a Teflon stirring bar, a thermometer, a rubber septum, and an inlet tube for argon, were placed chlorodifluoromethyl ketone 1 (1 mmol), dialkyl phosphite (1.2 mmol), triethylamine (1.2 mmol), and anhydrous THF (10 mL). The whole mixture was refluxed with stirring until the starting ketone 1 was consumed completely. ^{19}F NMR analysis for an aliquot of the reaction mixture revealed the completion of reaction after the reaction time cited in Table 1. The reaction was quenched with a saturated aqueous solution of ammonium chloride. The resulting mixture was extracted with diethyl ether and the ethereal extracts were dried over anhydrous sodium sulfate, followed by concentration under reduced pressure, to leave a residual oil. Column chromatography of the residue on silica gel afforded analytically pure product 2.

Diethyl 2,2-difluoro-1-methylethenyl phosphate (2a)

IR (film) 2970 (m), 2920 (m), 2840 (m), 1780 (m), 1440 (w), 1380 (w), 1270 (s), 1230 (s), 1140 (s), 1020 (s), 860 (m) cm^{-1}; ^1H NMR (CCl_4) δ 1.37 (t, J = 7.5 Hz, 6H), 1.89-2.00 (m, 3H), 4.07 (dq, J = 7.5 and 2.4 Hz, 4H); ^{19}F NMR (CCl_4) δ -22.8 (ddq, J = 84.7, 5.6, and 0.3 Hz, 1F), -37.7 (ddq, J = 84.7, 11.3, and 5.6 Hz, 1F); MS m/e (relative intensity) 230 (M^+, 8), 211 (2), 203 (10), 175 (9), 174 (36), 155 (9), 128 (15), 111 (35), 109 (29), 99 (100).

Diphenyl 2,2-difluoro-1-methylethenyl phosphate (2b)

80% yield; IR (film) 3070 (w), 3040 (w), 2960 (w), 2930 (w), 2850 (w), 1790 (s), 1595 (s), 1495 (s), 1290 (s), 1240 (s), 1205 (s), 1185 (s), 1160 (s), 1140 (s), 1015 (s), 965 (s), 875 (m), 770 (s), 755 (s), 685 (s) cm^{-1}; ^1H NMR (CCl_4) δ 1.92 (ddd, J = 4.5, 4.2, and 1.7 Hz, 3H), 7.00-7.35 (m, 10H); ^{19}F NMR (CCl_4) δ -19.4 (ddq, J = 67.7, 6.8, and 4.2 Hz, 1F), -35.1 (ddq, J = 67.7, 9.9, and 4.5 Hz, 1F); MS m/e (relative

intensity) 326 (M^+, 52), 307 (23), 255 (4.6), 254 (36), 253 (41), 219 (19), 174 (25), 98 (100), 81 (80).

Diethyl 2,2-difluoro-1-hexylethenyl phosphate (2c)

65% yield; IR (film) 2950 (s), 2920 (s), 2850 (m), 1770 (s), 1450 (m), 1390 (w), 1370 (w), 1270 (s), 1220 (s), 1160 (m), 1130 (m), 1030 (s), 980 (s), 900 (m), 810 (w) cm^{-1}; ^1H NMR (CCl_4) δ 0.75-1.37 (m, 11H), 1.36 (t, J = 7.2 Hz, 6H), 2.09-2.43 (m, 2H), 4.11 (dq, J = 7.2 and 8.6 Hz, 4H); ^{19}F NMR (CCl_4) δ -22.7 (ddt, J = 69.9, 7.1, and 2.5 Hz, 1F), -37.1 (ddt, J = 69.9, 9.2, and 3.5 Hz, 1F); MS m/e (relative intensity) 300 (M^+, 2.3), 285 (2.6), 271 (2.3), 244 (7.9), 217 (12), 173 (25), 155 (100), 127 (75), 99 (97).

Diphenyl 2,2-difluoro-1-hexylethenyl phosphate (2d)

64% yield; IR (film) 2950 (m), 2920 (m), 2850 (w), 1770 (w), 1590 (m), 1490 (m), 1280 (s), 1180 (s), 1150 (m), 1060 (m), 1020 (m), 1000 (m), 960 (s), 750 (m), 680 (m) cm^{-1}; ^1H NMR (CCl_4) δ 0.78-1.63 (m, 11H), 2.10-2.29 (m, 2H), 7.08-7.45 (m, 10H); ^{19}F NMR (CCl_4) δ -19.3 (ddt, J = 66.3, 6.8, and 2.3 Hz, 1F), -34.7 (ddt, J = 66.3, 9.3, and 3.7 Hz, 1F); MS m/e (relative intensity) no parent to 396, 249 (2.2), 160 (8.3), 113 (25), 105 (8.8), 95 (12), 94 (100).

Diethyl 1-cyclohexyl-2,2-difluoroethenyl phosphate (2e)

IR (film) 2990 (s), 2860 (s), 1770 (s), 1480 (m), 1450 (s), 1395 (m), 1375 (m), 1280 (s), 1240 (s), 1030 (s) cm^{-1}; ^1H NMR (CCl_4) δ 0.83-2.00 (m, 10H), 1.37 (t, J = 7.5 Hz, 6H), 2.15-2.40 (m, 1H), 4.10 (dq, J = 7.5 and 7.5 Hz, 4H); ^{19}F NMR (CCl_4) δ -20.3 (dd, J = 67.7 and 6.2 Hz, 1F), -33.1 (ddd, J = 67.7, 10.2, and 4.0 Hz, 1F); MS m/e (relative intensity) 298 (M^+, 8.2), 272 (2.5), 243 (1.3), 242 (1.3), 199 (2.5), 166 (4.4), 155 (81), 144 (15), 127 (72), 109 (14), 99 (100).

Diphenyl 1-cyclohexyl-2,2-difluoroethenyl phosphate (2f)

77% yield; IR (film) 2940 (s), 2850 (s), 1770 (s), 1590 (s), 1490 (s), 1450 (m), 1310 (s), 1290 (s), 1240 (s), 1200 (s), 1190 (s), 1160 (s), 1110 (s), 1070 (s), 1020 (s), 1010 (s), 950 (s), 840 (m), 770 (s), 750 (s), 690 (s) cm^{-1}; ^1H NMR

(CCl_4) δ 0.88-1.88 (m, 10H), 2.05-2.42 (m, 1H), 7.21 (m, 10H); ^{19}F NMR (CCl_4) δ -18.5 (dd, J = 66.0 and 7.1 Hz, 1F), -34.1 (ddd, J = 66.0, 9.6, and 4.0 Hz, 1F); MS m/e (relative intensity) 394 (M^+, 5.7), 252 (14), 251 (100), 250 (35), 170 (9.5), 144 (6.8), 129 (5.2), 94 (20), 77 (28).

Diethyl 1-benzyl-2,2-difluoroethenyl phosphate (2g)

73% yield; IR (film) 2980 (m), 2930 (m), 1750 (s), 1600 (w), 1500 (m), 1480 (w), 1455 (m), 1395 (w), 1285 (s), 1240 (s), 1190 (m), 1160 (m), 1090 (s), 1030 (s), 970 (s), 860 (w), 770 (w) cm^{-1}; ^1H NMR (CCl_4) δ 1.30 (t, J = 7.5 Hz, 6H), 3.58-3.72 (m, 2H), 3.97 (dq, J = 7.5 and 7.5 Hz, 4H), 7.23 (s, 5H); ^{19}F NMR (CCl_4) δ -21.0 (ddt, J = 59.3, 6.8, and 2.5 Hz, 1F), -35.2 (ddt, J = 59.3, 9.0, and 4.5 Hz, 1F); MS m/e (relative intensity) 306 (M^+, 20), 258 (1.6), 257 (1.6), 230 (4.2), 155 (100), 152 (35), 151 (39), 127 (44), 99 (48).

Diphenyl 1-benzyl-2,2-difluoroethenyl phosphate (2h)

62% yield; IR (film) 3070 (m), 3040 (m), 1780 (s), 1600 (s), 1495 (s), 1460 (m), 1290 (s), 1245 (s), 1190 (s), 1160 (s), 1090 (s), 1070 (s), 1030 (s), 1010 (s), 970 (s), 860 (m), 775 (s), 710 (m), 690 (s) cm^{-1}; ^1H NMR (CCl_4) δ 3.57-3.71 (m, 2H), 6.95-7.32 (m, 15H); ^{19}F NMR (CCl_4) δ -18.5 (ddt, J = 61.8, 7.1, and 2.3 Hz, 1F), -33.8 (ddt, J = 61.8, 9.9, and 3.4 Hz, 1F); MS m/e (relative intensity) 402 (M^+, 32), 382 (6.3), 255 (15), 254 (87), 253 (100), 174 (29), 156 (22), 155 (24), 98 (76), 81 (41).

Diethyl 2,2-difluoro-1-phenylethenyl phosphate (2i)

79% yield; IR (film) 2970 (m), 2900 (m), 1730 (m), 1590 (w), 1440 (w), 1390 (w), 1360 (w), 1270 (s), 1140 (s), 1010 (s), 980 (s), 890 (m) cm^{-1}; ^1H NMR (CCl_4) δ 1.57 (dt, J = 8.1 and 6.3 Hz, 6H), 4.17 (dq, J = 11.5 and 6.3 Hz, 4H), 7.13-7.55 (m, 5H); ^{19}F NMR (CCl_4) δ -17.6 (dd, J = 57.9 and 7.1 Hz, 1F), -30.8 (dd, J = 57.9 and 11.3 Hz, 1F); MS m/e (relative intensity) 292 (M^+, 22), 264 (12), 244 (11), 236 (32), 235 (19), 216 (71), 156 (12), 155 (30), 105 (100), 101 (21), 91 (16), 81 (23), 77 (56).

Diphenyl 2,2-difluoro-1-phenylethenyl phosphate (2j)

73% yield; IR (film) 3050 (w), 1730 (m), 1590 (s), 1490 (s), 1480 (s), 1440 (w), 1270 (s), 1210 (s), 1180 (s), 1150 (s), 1120 (s), 1060 (m), 1020 (s), 1000 (s), 940 (s), 730 (w), 680 (s) cm^{-1}; ^1H NMR (CCl_4) δ 6.94-7.62 (m, 15H); MS m/e (relative intensity) no parent to 388, 264 (0.2), 217 (0.4), 216 (0.6), 173 (1), 156 (4), 105 (49), 94 (100), 77 (38).

Reaction of ketone **1** with diethyl phosphite at 0-20 °C giving rise to 1-(chlorodifluoromethyl)-1-hydroxyalkanephosphonate **3**

The reaction was conducted in anhydrous diethyl ether at 0-20 °C. The procedure and other reaction conditions were the same as those in the above-described reaction leading to enol phosphates **2**.

Diethyl 1-(chlorodifluoromethyl)-1-hydroxyethanephosphonate (3a)

IR (film) 3220 (br s), 2970 (s), 2910 (s), 1440 (m), 1390 (m), 1230 (s), 1110 (s), 1010 (s), 950 (s) cm^{-1}; ^1H NMR (CCl_4) δ 1.28 (t, J = 7.8 Hz, 6H), 1.53 (d, J = 15.0 Hz, 3H), 4.11 (dq, J = 7.2 and 7.2 Hz, 4H); ^{19}F NMR (CCl_4) δ 18.8 (d, J = 6.8 Hz, 2F); MS m/e (relative intensity) no parent to 266, 230 (5.4), 203 (6.5), 175 (6.5), 174 (27), 127 (14), 111 (100), 99 (43), 93 (48), 83 (100), 81 (43).

Diethyl 1-(chlorodifluoromethyl)-1-hydroxyheptanephosphonate (3b)

IR (film) 3220 (br s), 2950 (s), 2920 (s), 2850 (s), 1460 (m), 1390 (w), 1230 (s), 1020 (s), 970 (s), 780 (m) cm^{-1}; ^1H NMR (CCl_4) δ 0.87 (t, J ≈ 4.5 Hz, 3H), 1.10-2.10 (m, 10H), 1.33 (t, J ≈ 7.5 Hz, 6H), 4.13 (dq, J = 7.5 and 7.5 Hz, 4H), 5.28 (s, 1H); ^{19}F NMR (CCl_4) δ 19.5 and 21.5 (two s, 1F), 22.2 and 24.2 (two s, 1F); MS m/e (relative intensity) no parent to 336, 300 (0.3), 285 (0.3), 244 (0.6), 173 (3.1), 155 (11), 114 (18), 113 (100), 111 (59), 99 (12), 85 (39).

Diethyl 2-chloro-1-cyclohexyl-2,2-difluoro-1-hydroxyethanephosphonate (**3c**)

IR (film) 3250 (br s), 2980 (s), 2930 (s), 2850 (s), 1455 (m), 1445 (m), 1395 (m), 1270 (m), 1245 (s), 1165 (s), 1100 (s), 1025 (s), 1015 (s) cm^{-1}; ^1H NMR (CCl_4) δ 0.93-2.33 (m, 11H), 1.37 (dt, J = 7.5 and 2.4 Hz, 6H), 4.17 (dq, J = 7.5 and 7.5 Hz, 4H), 5.30 (br s, 1H); ^{19}F NMR (CCl_4) δ 23.3 and 25.3 (two d, J = 3.4 Hz, 1F), 27.3 and 29.3 (two s, 1F); MS m/e (relative intensity) no parent to 334, 298 (0.8), 205 (0.5), 155 (21), 129 (5), 127 (15), 111 (63), 99 (15), 83 (100).

Diethyl 1-(chlorodifluoromethyl)-1-hydroxy-2-phenylethanephosphonate (**3d**)

IR (film) 3220 (br s), 2990 (s), 2930 (m), 1605 (w), 1500 (m), 1480 (m), 1455 (m), 1445 (m), 1395 (m), 1370 (m), 1265 (s), 1235 (s), 1100 (s), 1020 (s), 900 (m), 785 (s), 760 (s), 700 (s) cm^{-1}; ^1H NMR (CCl_4) δ 1.13 (t, J = 7.8 Hz, 3H), 1.30 (t, J = 7.8 Hz, 3H), 4.07 (dq, J = 7.8 and 7.8 Hz, 4H), 5.77-6.33 (br s, 1H), 7.00-7.37 (m, 5H); ^{19}F NMR (CCl_4) δ 20.3 and 22.2 (two s, 1F), 23.4 and 25.3 (two d, J = 2.8 Hz, 1F); MS m/e (relative intensity) no parent to 342, 306 (1.4), 210 (4.9), 208 (15), 123 (16), 105 (35), 95 (100), 87 (37).

Diethyl 2-chloro-2,2-difluoro-1-hydroxy-1-phenylethanephosphonate (**3e**)

IR (film) 3230 (br s), 2970 (s), 2900 (s), 1600 (w), 1490 (m), 1470 (m), 1440 (m), 1390 (m), 1360 (m), 1230 (s), 1160 (s), 1100 (s), 1030 (s) cm^{-1}; ^1H NMR (CCl_4) δ 1.15 (t, J = 6.0 Hz, 3H), 1.39 (dt, J = 5.4 and 3.0 Hz, 3H), 4.13 (dq, J = 7.2 and 4.2 Hz, 4H), 5.87 (s, 1H), 6.97-8.27 (m, 5H); ^{19}F NMR (CCl_4) δ 19.0 and 20.8 (two s, 1F), 21.7 and 23.5 (two s, 1F); MS m/e (relative intensity) 328 (M^+, 0.1), 293 (5.3), 265 (2.5), 237 (6.3), 217 (12), 112 (52), 106 (100), 94 (14), 84 (56).

Treatment of 3 with a base in refluxing THF

A mixture of **3** (1 mmol) and triethylamine or sodium methoxide (1.2 mmol) in THF (10 mL) was refluxed under argon

for 20 h. The reaction mixture was poured into water, followed by extraction with diethyl ether, drying with anhydrous sodium sulfate, and concentration in vacuo. The crude product was chromatographed on silica gel to give the corresponding enol phosphate 2 in 80-90% yield.

The reaction without the base resulted in a quantitative recovery of 3.

Reaction between chlorodifluoromethyl ketone 1 and sodium diethyl phosphite

To a suspension of sodium hydride (1.2 mmol) in anhydrous diethyl ether (10 mL) was dropwise added diethyl phosphite (1.2 mmol) at 0 °C under an argon atmosphere. After stirring for 1 h, chlorodifluoromethyl ketone 1 (1 mmol) was added to the resultant mixture at 0 °C. This reaction mixture was stirred at ambient temperature for 20 h, and then was treated with a saturated aqueous solution of ammonium chloride. The mixture was subjected to extraction with ether, drying over anhydrous sodium sulfate, and concentration under vacuum. Silica-gel column chromatography of the residue afforded pure product 2 in a yield of 70-80%.

Reaction of ketone 1 with triethyl phosphite

A solution of ketone 1 (1 mmol) and triethyl phosphite (1.1 mmol) in anhydrous THF (10 mL) was refluxed with stirring under argon. After 20 h, the reaction mixture was concentrated under reduced pressure to remove the solvent and volatile materials. The residual oil was column-chromatographed on silica gel to give 2,2-difluoroethenyl phosphate 2 in a good yield.

REFERENCES

1 W. Perkow, K. Ullerich and F. Meyer, Naturwissenschaften, 39 (1952) 353. F.W. Lichtenthaler, Chem. Rev., 61 (1961) 607. A.J. Kirby and S.G. Warren, 'The Organic Chemistry of Phosphorus,' Elsevier, New York (1967).

2 B.A. Arbuzov, V.S. Vinogradova and N.A. Polezhaeva, Dokl. Akad. Nauk SSSR, 121 (1958) 641; Chem. Abstr., 53 (1959) 1180.

3 G. Sturtz, Bull. Soc. Chim. Fr., (1964) 2333.

4 A. Meisters and J.M. Swan, Aust. J. Chem., 18 (1965) 168.

5 D. Redmore, Chem. Rev., 71 (1971) 315. B. Springs and P. Haake, J. Org. Chem., 41 (1976) 1165.

6 M. Sekine, K. Okimoto, K. Yamada and T. Hata, J. Org. Chem., 46 (1981) 2097. M. Sekine, M. Nakajima and T. Hata, ibid., 46 (1981) 4030.

7 E.E. Gilbert, J.A. Otto and J.J. Donleavy, U.S. Pat. 2 929 759 (1960); Chem. Abstr., 54 (1960) 18362f. K. Szabo, U.S. Pat. 3 170 944 (1965); Chem. Abstr., 62 (1965) 13180d. N.P. Gambaryan, E.M. Rokhlin, Y.V. Zeifman, C.Y. Chen and I.L. Knunyants, Angew. Chem. Int. Ed. Engl., 5 (1966) 947. A.F. Janzen and R. Pollitt, Can. J. Chem., 48 (1970) 1987. I.L. Knunyants, Y.A. Sizov and O.U. Ukharov, Usp. Khim., 52 (1983) 976; Chem. Abstr., 99 (1983) 70148.

8 (a) T. Ishihara, H. Shinjo, Y. Inoue and T. Ando, J. Fluorine Chem., 22 (1983) 1. (b) M. Yamana, T. Ishihara and T. Ando, Tetrahedron Lett., 24 (1983) 507. (c) T. Ishihara, T. Maekawa and T. Ando, ibid., 24 (1983) 4229. (d) T. Ishihara, M. Yamana and T. Ando, ibid., 24 (1983) 5657. (e) T. Ishihara, T. Maekawa and T. Ando, ibid., 25 (1984) 1377. (f) T. Ishihara, T. Yamanaka and T. Ando, Chem. Lett., (1984) 1165. (g) T. Ishihara, T. Maekawa and T. Ando, Tetrahedron Lett., 27 (1986) 357. (h) T. Ishihara and M. Kuroboshi, Chem. Lett., (1987) 1145. (i) T. Ishihara, T. Maekawa, Y. Yamasaki and T. Ando, J. Org. Chem., 52 (1987) 300. (j) M. Kuroboshi, Y. Okada, T. Ishihara and T. Ando, Tetrahedron Lett., 28 (1987) 3501.

9 T. Ishihara, T. Maekawa, Y. Yamasaki and T. Ando, J. Fluorine Chem., 34 (1986) 271. Idem, ibid., 34 (1987) 323.

10 T. Ishihara, Y. Yamasaki and T. Ando, Tetrahedron Lett., 27 (1986) 2879.

11 A. Sykes, J.C. Tatlow and C.R. Thomas, J. Chem. Soc., (1956) 835. R.A. Moore and R. Levine, J. Org. Chem., 29 (1964) 1439.

12 V.S. Abramov and R.N. Savintseva, Khim. Org. Soedin. Fosfora, Akad. Nauk, (1967) 129; Chem. Abstr., 69 (1968) 67465. T. Agawa, T. Kubo and Y. Ohshiro, Synthesis, (1971) 27.

13 I.J. Borowitz, S. Firstenberg, G.B. Borowitz and D. Schuessler, J. Am. Chem. Soc., 94 (1972) 1623. E.M. Gaydou and J.P. Bianchini, Can. J. Chem., 54 (1976) 3626.

14 T. Ishihara and M. Kuroboshi, unpublished results.