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Synthesis of Non-Symmetric Functionalized Polyfluoroalkyl Phosphites

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Abstract—Two ways for the synthesis of new representatives of non-symmetric organic phosphites with polyfluoroalkyl substituents were developed based on organic dichlorophosphites. The reaction of polyfluoroalkyl dichlorophosphites with allyl alcohol, proceeding at a temperature of –10–22°C (2 h) in the presence of triethylamine, gave diallyl polyfluoroalkyl phosphites in a yield of 75–77%. Under similar conditions (–30–22°C, 2–4 h, Et_3N), alkyl (or aryl) dichlorophosphites reacted with polyfluoroalkanols to form alkyl (or aryl) bis(polyfluoroalkyl) phosphites (yield 56–67%). Unlike diallylpolyfluoroalkyl- and alkylbis(polyfluoroalkyl) phosphites, arylbis(polyfluoroalkyl)-phosphites are symmetrized under storage conditions (room temperature, inert atmosphere), forming the corresponding triaryl- and tris(polyfluoroalkyl) phosphites.

Keywords: dichlorophosphites, allyl alcohol, polyfluoroalkanols, diallyl polyfluoroalkyl phosphites, alkylbis(polyfluoroalkyl) phosphites, arylbis(polyfluoroalkyl) phosphites

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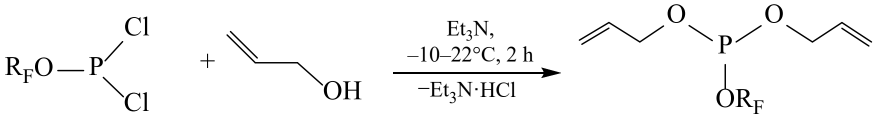
In recent years, special attention of researchers has been given to fluorinated organic phosphites, which are used as additives in lithium-ion battery electrolytes to increase their fire and explosion safety [1–7], as well as drug precursors [8–11], ligands for special metal complexes [12–18], reactive building blocks for organic synthesis [10, 11, 19–25]. Typical methods for the synthesis of fluorine-substituted phosphites are based on the use of phosphorus trichloride or diorganyl chlorophosphites as phosphorylating reagents of alkanols [10–12, 20, 22, 26]. Organic dichlorophosphites have been much less studied in these reactions [27–30]. Polyfluoroalkylphosphites with allyl substituents are also unknown; however the introduction of these moieties allows the use of such compounds in the synthesis of promising non-combustible polymeric materials [7].

Herein, we reported a convenient method for the synthesis of new representatives of non-symmetric functionalized polyfluoroalkyl phosphites based on the reactions of polyfluoroalkyl dichlorophosphites with allyl alcohol and organic dichlorophosphites with polyfluoroalkanols.

Polyfluoroalkyl dichlorophosphites **1a**–**1c** reacted with allyl alcohol under mild conditions (–10–22°C, 2 h, CH_2Cl_2 or Et_2O) in the presence of triethylamine to furnish diallyl polyfluoroalkyl phosphites **2a**–**2c** with a yield of 75–77% (Scheme 1). The reaction proceeded chemoselectively: no prototropic isomerization of the allyl fragment to prop-1-enyl under the indicated conditions was observed (^{31}P NMR data). Compounds **2a**–**2c** are stable during storage in an inert atmosphere and do not undergo symmetrization with the formation of triallyl and tris(polyfluoroalkyl) phosphites.

The developed method allows us to synthesize new representatives of non-symmetric polyfluoroalkyl phosphites starting from dichlorophosphites **3a**–**3c** and fluoroalkanols **4**, **5**. Under similar conditions (Et_3N, an organic solvent, –10–22°C for ethyl dichlorophosphite **3a** and –30–22°C for aryl phosphites **3b**, **3c**) the reaction proceeded within 2–4 h to afford organyl

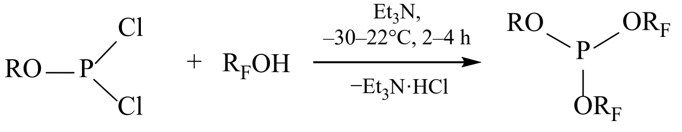
Scheme 1.



1a–**1c** **2a**–**2c** (75–77%)

$R_F = CF_3CH_2$ (**a**), $H(CF_2)_2CH_2$ (**b**), $H(CF_2)_4CH_2$ (**c**).

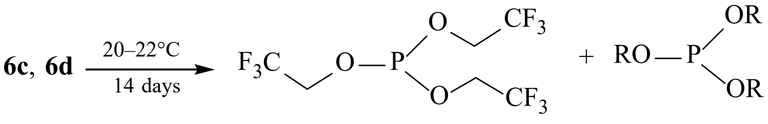
Scheme 2.



3a–**3c** **4**, **5** **6a**–**6d** (56–67%)

R = Et (**3a**, **6a**, **6b**), 4-$MeOC_6H_4$ (**3b**, **6c**), 4-FC_6H_4 (**3c**, **6d**);
$R_F = CF_3CH_2$ (**4**, **6a**, **6c**, **6d**), $H(CF_2)_4CH_2$ (**5**, **6b**).

Scheme 3.



7 **8**, **9**

R = 4-$MeOC_6H_4$ (**6c**, **8**), 4-FC_6H_4 (**6d**, **9**).

bis(polyfluoroalkyl) phosphites **6a**–**6d** with a moderate yield of 56–67% (Scheme 2).

Alkyl phosphites **6a** and **6b** derived from ethyl dichlorophosphite **3a** are relatively stable upon standing under standard conditions (room temperature, argon, 14 days), while 4-methoxyphenyl and 4-fluorophenyl phosphites **6c** and **6d** under the same conditions undergo conversions with the formation of symmetric tris(trifluoroethyl) phosphite **7** and triaryl phosphites **8**, **9** (Scheme 3). Within two weeks, the compounds ratio was **6c** : **7** : **8** = 24 : 1 : 0.5 and **6d** : **7** : **9** = 24 : 2 : 1 (by ^1H, ^{31}P NMR data).

New representatives of non-symmetric functionalized triorganyl phosphites with polyfluoroalkyl substituents obtained by a convenient effective method can be used as components for lithium-ion batteries, drug precursors, and ligands for the production of metal complexes.

EXPERIMENTAL

^1H, ^{13}C, ^{19}F, ^{31}P NMR spectra were obtained on a Bruker DPX 400 and a Bruker AV-400 spectrometers (400.13, 101.61, 376.50, and 161.98 MHz, respectively) from $CDCl_3$ solutions relative to internal HMDS (^1H, ^{13}C), $CFCl_3$ (^{19}F), and external 85% H_3PO_4 (^{31}P). IR spectra were recorded on a Bruker IFS 25 spectrometer from thin layer.

The starting polyfluoroalkyl dichlorophosphites **1a**–**1c** were obtained from PCl_3 and polyfluoroalkanols in the presence of triethylamine (1 mol %) [31]. The starting ethyl dichlorophosphite **3a** was synthesized according to the procedure [32]. Aryl dichlorophosphites **3b** and **3c** were obtained by a modified procedure [33] from PCl_3 and 4-substituted phenols (1.5 : 1). All experiments were carried out in a dry inert atmosphere (argon).

General procedure for the synthesis of diallyl polyfluoroalkyl phosphites 2a–2c. A solution of 40.3 mmol of polyfluoroalkyl dichlorophosphite **1** in 20 mL of dichloromethane was added dropwise with stirring for 1 h at –10–7°C to a solution of 89.5 mmol (6.45 g) of allyl alcohol and 93.9 mmol (9.5 g) of triethylamine in 60 mL of anhydrous dichloromethane. The formation of a white precipitate of triethylamine hydrochloride was observed. The reaction mixture was stirred for 1 h at room temperature, then 100 mL of hexane was added and the resulting mixture was kept overnight. Triethylamine hydrochloride was filtered off, washed with hexane (5 × 30 mL). Washings and the filtrate were combined, the solvents were distilled off under reduced pressure, and the residue was distilled in vacuum. Phosphite **2b** was synthesized in diethyl ether (120 mL).

Diallyl (2,2,2-trifluoroethyl) phosphite (2a). Yield 7.4 g (75%), clear liquid, bp 38–39°C (1 mmHg), d_4^{20} 1.1649, n_D^{20} 1.4013, η 1.37 cP. IR spectrum, ν, cm^{-1}: 3089 m, 3020 w, 2986 m, 2940 m, 2879 m, 1649 m, 1456 m, 1424 m, 1410 m, 1339 w, 1283 s, 1168 s, 1089 s, 1068 s, 1023 s, 988 s, 963 s, 924 s, 846 m, 794 s, 656 w, 558 w, 512 w. ^{1}H NMR spectrum, δ, ppm: 4.12 d. q (2H, CF_3CH_2, $^3J_{HP} = 7.1$, $^3J_{HF} = 8.4$ Hz), 4.36 d. d (4H, $C\mathbf{H}_2CH=$, $^3J_{HP} =$ 8.1, $^3J_{HH} = 5.4$ Hz), 5.19 d (2H, $=CH_2$, H_{cis}, $^3J_{cis} =$ 10.4 Hz), 5.30 d (2H, $=CH_2$, H_{trans}, $^3J_{trans} = 18.2$ Hz), 5.90 d. d. t (2H, CH=, $^3J_{trans} = 18.2$, $^3J_{cis} = 10.4$, $^3J_{HH}$ = 5.4 Hz). ^{13}C NMR spectrum, δ_C, ppm: 59.0 q. d ($CF_3\mathbf{C}H_2$, $^2J_{CF} = 36.2$, $^2J_{CP} = 8.6$ Hz), 63.6 d ($\mathbf{C}H_2CH=$, $^2J_{CP} = 12.1$ Hz), 116.8 ($CH_2=$), 123.4 q. d (CF_3, $^1J_{CF} =$ 278.0, $^3J_{CP} = 6.0$ Hz), 133.8 d (CH=, $^3J_{CP} = 5.2$ Hz). ^{19}F NMR spectrum: δ_F –75.3 ppm. ^{31}P NMR spectrum: δ_P 139.7 ppm. Found, %: C 39.12; H 4.78; F 23.48; P 12.48. $C_8H_{12}F_3O_3P$. Calculated, %: C 39.36; H 4.95; F 23.34; P 12.69.

Diallyl (2,2,3,3-tetrafluoropropyl) phosphite (2b). Yield 8.6 g (77%), clear colorless liquid, bp 59–60°C (1 mmHg), d_4^{20} 1.2067, n_D^{20} 1.4076, η 1.80 cP. IR spectrum, ν, cm^{-1}: 3089 m, 3020 m, 2988 s, 2946 s, 2880 s, 1650 m, 1458 s, 1425 s, 1416 m, 1380 m, 1359 m, 1282 s, 1265 s, 1230 s, 1210 s, 1130 s, 1105 s, 1051 s, 1022 s, 989 s, 932 s, 835 s, 793 s, 680 m, 673 w, 645 w, 583 w, 549 m, 385 w. ^{1}H NMR spectrum, δ, ppm: 3.96 t. d. t (2H, CH_2CF_2, $^3J_{HF} = 12.7$, $^3J_{HP} = 6.2$, $^4J_{HF} =$ 1.6 Hz), 4.17 d. d. t (4H, $C\mathbf{H}_2CH=$, $^3J_{HP} = 8.4$, $^3J_{HH} =$ 5.3, $^4J_{HH} = 1.6$ Hz), 5.03 d. m (2H, $=CH_2$, H_{cis}, $^3J_{cis} =$ 10.5 Hz), 5.20 d. d. t (2H, $=CH_2$, H_{trans}, $^3J_{trans} = 17.1$, $^2J_{HH} =$ 1.7, $^4J_{HH} = 1.6$ Hz), 5.52 t. t. d (1H, CF_2H, $^2J_{HF} = 53.1$, $^3J_{HF} = 4.9$, $^5J_{HP} = 1.5$ Hz), 5.75 d. d. t (2H, CH=, $^3J_{trans} =$ 17.1, $^3J_{cis} = 10.5$, $^3J_{HH} = 5.3$ Hz). ^{13}C NMR spectrum, δ_C, ppm: 58.8 t. d ($\mathbf{C}H_2CF_2$, $^2J_{CF} = 29.5$, $^2J_{CP} = 7.9$ Hz), 63.6 d ($\mathbf{C}H_2CH=$, $^2J_{CP} = 12.1$ Hz), 109.5 t. t (CF_2H, $^1J_{CF} =$ 249.3, $^2J_{CF} = 34.4$ Hz), 115.2 t. t. d ($CH_2\mathbf{C}F_2$, $^1J_{CF} =$ 249.7, $^2J_{CF} = 26.7$, $^3J_{CP} = 5.0$ Hz), 117.4 ($CH_2=$), 134.5 d (CH=, $^3J_{CP} = 5.1$ Hz). ^{19}F NMR spectrum, δ, ppm: –139.2 d. t (CF_2H, $^2J_{HF} = 53.1$, $^3J_{FF} = 4.6$ Hz), –125.7 m (CF_2). ^{31}P NMR spectrum: δ_P 139.5 ppm. Found, %: C 39.12; H 4.85; F 27.65; P 11.38. $C_9H_{13}F_4O_3P$. Calculated, %: C 39.14; H 4.74; F 27.52; P 11.22.

Diallyl (2,2,3,3,4,4,5,5-octafluoropentyl) phosphite (2c). Yield 11.4 g (75%), clear colorless liquid, bp 70–72°C (1 mmHg), d_4^{20} 1.3534, n_D^{20} 1.3882, η 3.63 cP. IR spectrum, ν, cm^{-1}: 3090 m, 3021 m, 2988 m, 2954 m, 2889 m, 1650 m, 1459 m, 1426 m, 1411 m, 1360 m, 1287 s, 1263 s, 1173 s, 1132 s, 1023 s, 988 s, 928 s, 904 s, 806 s, 689 w, 673 w, 628 m, 609 m, 546 m, 506 m. ^{1}H NMR spectrum, δ, ppm: 4.24 t. d. t (2H, $C\mathbf{H}_2CF_2$, $^3J_{HF} =$ 14.0, $^3J_{HP} = 6.5$, $^4J_{HF} = 1.4$ Hz), 4.36 d. d. d. d (4H, $C\mathbf{H}_2CH=$, $^3J_{HP} = 8.4$, $^3J_{HH} = 5.4$, $^4J_{HH} = 1.4$, $^4J_{HH} =$ 0.7 Hz), 5.19 d. d. d. d (2H, $=CH_2$, H_{cis}, $^3J_{cis} = 10.4$, $^2J_{HH} = 1.5$, $^4J_{HH} = 1.4$, $^4J_{HH} = 0.7$ Hz), 5.28 d. d. t (2H, $=CH_2$, H_{trans}, $^3J_{trans} = 17.1$, $^2J_{HH} = 1.5$, $^4J_{HH} = 1.4$ Hz), 5.91 d. d. t (2H, CH=, $^3J_{trans} = 17.1$, $^3J_{cis} = 10.4$, $^3J_{HH} =$ 5.4 Hz), 6.03 t. t (1H, CF_2H, $^2J_{HF} = 51.9$, $^3J_{HF} = 5.4$ Hz). ^{13}C NMR spectrum, δ_C, ppm: 58.4 t. d ($\mathbf{C}H_2CF_2$, $^2J_{CF} =$ 26.3, $^2J_{CP} = 8.2$ Hz), 63.9 d ($\mathbf{C}H_2CH=$, $^2J_{CP} =$ 12.1 Hz), 107.7 t. t (CF_2H, $^1J_{CF} = 254.0$, $^2J_{CF} = 31.0$ Hz), 110.1 t. q ($\mathbf{C}F_2CF_2H$, $^1J_{CF} = 250.0$, $^2J_{CF} = 29.0$ Hz), 110.9 t. q ($\mathbf{C}F_2CF_2CF_2H$, $^1J_{CF} = 264.7$, $^2J_{CF} = 30.6$ Hz), 115.1 t. t. d ($\mathbf{C}F_2CH_2$, $^1J_{CF} = 256.5$, $^2J_{CF} = 31.0$, $^3J_{CP} =$ 3.5 Hz), 117.0 ($CH_2=$), 134.1 d (CH=, $^3J_{CP} = 5.2$ Hz). ^{19}F NMR spectrum, δ_F, ppm: –137.2 d (CF_2H, $^2J_{HF} =$ 51.9 Hz), –130.2 m ($C\mathbf{F}_2CF_2H$), –125.3 m ($C\mathbf{F}_2CF_2CF_2H$), –120.4 m (CF_2CH_2). ^{31}P NMR spectrum: δ_P 140.8 ppm. Found, %: C 35.10; H 3.47; F 40.18; P 8.10. $C_{11}H_{13}F_8O_3P$. Calculated, %: C 35.12; H 3.48; F 40.40; P 8.23.

General procedure for the synthesis of organyl bis(polyfluoroalkyl) phosphites 6a–6d. To a solution of 64.7 mmol of organyl dichlorophosphite **3** in 150 mL of an organic solvent [diethyl ether (**3a**), dichloromethane (60 mL) (**3b**), hexane (**3c**, **3d**)] was added dropwise with stirring a solution of 155 mmol of polyfluoroalkanol **4** or **5** and 155 mmol (15.7 g) of triethylamine in 30 mL of the corresponding solvent for 1–2 h at low temperature [–10–8°C (**3a**, **3b**), –30–25°C (**3c**, **3d**), dry ice–acetone]. The formation of a white precipitate of triethylamine hydrochloride was observed. The reaction mixture was stirred for 1–2 h at room temperature, argon was passed to remove HCl, and the mixture was kept overnight in the case of obtaining compounds **6a** and **6b**. The precipitate (triethylamine hydrochloride) was filtered off, washed (3 × 30 mL) with diethyl ether (**3a**) or hexane (**3b**–**3d**). Washings and the filtrate were combined, the solvents were distilled off under reduced pressure, and the residue was distilled in vacuum. To prevent symmetrization of the aryl bis(polyfluoroalkyl) phosphites **6c** and **6d**, the distillation flask was placed into a heated glycerin bath (100–120°C) and distillation was carried out rapidly.

Bis(2,2,2-trifluoroethyl) ethyl phosphite (6a). Yield 9.9 g (56%), clear colorless liquid, bp 23°C (1 mmHg), d_4^{20} 1.3743, n_D^{20} 1.3022, η 1.92 cP. IR spectrum, ν, cm^{-1}: 2980 m, 2950 m, 2921 m, 2880 w, 2854 w, 1806 w, 1483 m, 1458 m, 1424 s, 1400 m, 1375 m, 1273 s, 1174 s, 1083 s, 1041 s, 965 s, 894 s, 842 s, 769 m, 661 s, 559 m, 510 m, 483 m. ^{1}H NMR spectrum, δ, ppm: 1.28 t (3H, CH_3, $^3J_{HH}$ = 7.1 Hz), 3.95 d. q (2H, $CH_3C\mathbf{H}_2$, $^3J_{HP}$ = 8.4, $^3J_{HH}$ = 7.1 Hz), 4.13 q (4H, $CF_3C\mathbf{H}_2$, $^3J_{HF}$ = $^3J_{HP}$ = 8.4 Hz). ^{13}C NMR spectrum, δ_C, ppm: 16.4 d (CH_3, $^3J_{CP}$= 5.2 Hz), 59.5 q. d ($CF_3\mathbf{C}H_2$, $^2J_{CF}$ = 36.9, $^2J_{CP}$ = 9.6 Hz), 59.9 d ($CH_3\mathbf{C}H_2$, $^2J_{CP}$ = 12.5 Hz), 123.4 q. d (CF_3, $^1J_{CF}$ = 277.9, $^3J_{CP}$ = 5.9 Hz). ^{19}F NMR spectrum, δ_F, ppm: –75.5 t. d (CF_3, $^3J_{FH}$ = 8.4, $^4J_{FP}$ = 4.5 Hz). ^{31}P NMR spectrum: δ_P 139.5 ppm. Found, %: C 26.08; H 3.51; F 41.33; P 11.50. $C_6H_9F_6O_3P$. Calculated, %: C 26.29; H 3.31; F 41.59; P 11.30.

Bis(2,2,3,3,4,4,5,5-octafluoropentyl) ethyl phosphite (6b). Yield 22.6 g (65%), clear colorless liquid, bp 105°C (1 mmHg), d_4^{20} 1.3466, n_D^{20} 1.5876, η 9.49 cP. IR spectrum, ν, cm^{-1}: 2989 m, 2950 m, 2897 m, 1481 w, 1457 m, 1402 m, 1395 m, 1361 m, 1331 m, 1291 s, 1172 s, 1133 s, 1058 s, 1030 s, 991 s, 958 s, 940 s, 904 s, 873 m, 806 s, 717 m, 690 m, 674 w, 629 m, 609 m, 546 m, 523 m, 453 w, 446 w. ^{1}H NMR spectrum, δ, ppm: 1.30 t (3H, CH_3, $^3J_{HH}$ = 7.1 Hz), 3.98 d. q (2H, $CH_3C\mathbf{H}_2$, $^3J_{HP}$ = 8.4, $^3J_{HH}$ = 7.1 Hz), 4.27 t. d (4H, $CF_2C\mathbf{H}_2$, $^3J_{HF}$ = 13.5, $^3J_{HP}$ = 6.6 Hz), 6.05 t. t (2H, CF_2H, $^2J_{HF}$ = 52.2, $^3J_{HF}$ = 5.5 Hz). ^{13}C NMR spectrum, δ_C, ppm: 16.6 d (CH_3, $^3J_{CP}$ = 5.2 Hz), 58.9 t. d ($CF_2\mathbf{C}H_2$, $^2J_{CF}$ = 26.4, $^2J_{CP}$ = 9.2 Hz), 60.2 d ($CH_3\mathbf{C}H_2$, $^2J_{CP}$ = 13.2 Hz), 107.8 t. t (CF_2H, $^1J_{CF}$ = 253.7, $^2J_{CF}$ = 31.2 Hz), 111.1 t. q ($CF_2\mathbf{C}F_2\mathbf{C}F_2CF_2H$, $^1J_{CF}$ = 265.2, $^2J_{CP}$ = 31.2 Hz), 115.0 t. t. d ($OCH_2\mathbf{C}F_2$, $^1J_{CF}$ = 256.8, $^2J_{CF}$ = 31.6, $^3J_{CP}$ = 4.4 Hz). ^{19}F NMR spectrum, δ_F, ppm: –137.4 d. m (CF_2H, $^2J_{HF}$ = 52.0 Hz), –130.3 m ($C\mathbf{F}_2CF_2H$), –125.5 m ($C\mathbf{F}_2CF_2CF_2H$), –120.7 m (CH_2CF_2). ^{31}P NMR spectrum: δ_P 139.8 ppm. Found, %: C 26.68; H 2.11; F 56.33; P 5.55. $C_{12}H_{11}F_{16}O_3P$. Calculated, %: C 26.78; H 2.06; F 56.48; P 5.76.

4-Methoxyphenyl bis(2,2,2-trifluoroethyl) phosphite (6c). Yield 15.3 g (67%), clear colorless liquid, bp 99–100°C (1 mmHg), d_4^{20} 1.4181, n_D^{20} 1.4314, η 5.27 cP. IR spectrum, ν, cm^{-1}: 3120 w, 3048 w, 3006 m, 2964 s, 2915 m, 2841 m, 1609 w, 1593 m, 1506 s, 1467 s, 1456 s, 1444 s, 1413 s, 1283 s, 1250 s, 1207 s, 1167 s, 1090 s, 1058 s, 1036 s, 1009 m, 963 s, 925 m, 886 s, 848 s, 834 s, 797 s, 720 m, 698 m, 654 s, 637 w, 567 m, 548 s, 534 w, 522 s, 496 w. ^{1}H NMR spectrum, δ, ppm: 3.71 s (3H, CH_3), 4.30 q (4H, CH_2, $^3J_{HP}$ = $^3J_{HF}$ = 8.3 Hz), 6.87 d (2H, C_6H_4, $^3J_{HH}$ = 8.9 Hz), 6.99 d (2H, C_6H_4, $^3J_{HH}$ = 8.9 Hz). ^{13}C NMR spectrum, δ_C, ppm: 55.4 (CH_3), 59.5 q. d (CH_2, $^2J_{CF}$ = 36.9, $^2J_{CP}$ = 7.6 Hz), 114.8 ($C^{3,5}$, C_6H_4), 121.0 d ($C^{2,6}$, C_6H_4, $^3J_{CP}$ = 6.7 Hz), 123.5 q. d (CF_3, $^1J_{CF}$ = 275.3, $^3J_{CP}$ = 5.3 Hz), 144.4 d (C^1, C_6H_4, $^2J_{CP}$ = 6.9 Hz), 156.5 (C^4, C_6H_4). ^{19}F NMR spectrum, δ_F, ppm: –75.3 t. d (CF_3, $^3J_{FH}$ = 8.2, $^4J_{FP}$ = 4.0 Hz). ^{31}P NMR spectrum: δ_P 132.5 ppm. Found, %: C 37.40; H 2.96; F 32.10; P 8.68. $C_{11}H_{11}F_6O_4P$. Calculated, %: C 37.52; H 3.15; F 32.37; P 8.80.

Bis(2,2,2-trifluoroethyl) (4-fluorophenyl) phosphite (6d). Yield 14.6 g (66%), clear colorless liquid, bp 65–68°C (2 mmHg), d_4^{20} 1.4590, n_D^{20} 1.4082, η 2.89 cP. IR spectrum, ν, cm^{-1}: 3119 w, 3084 w, 3057 m, 2968 s, 2892 m, 1602 w, 1505 s, 1455 s, 1413 s, 1305 w, 1284 s, 1199 s, 1171 s, 1091 s, 1060 s, 1013 s, 964 s, 932 m, 888 s, 848 s, 841 s, 812 s, 718 m, 695 m, 654 s, 633 w, 564 m, 548 s, 534 , 513 s, 477 m, 449 w. ^{1}H NMR spectrum, δ, ppm: 4.30 q (4H, CH_2, $^3J_{HF}$ = $^3J_{HP}$ = 8.3 Hz), 7.03 m (4H, C_6H_4). ^{13}C NMR spectrum, δ_C, ppm: 60.2 q. d (CH_2, $^2J_{CF}$ = 36.8, $^2J_{CP}$ = 7.7 Hz), 116.6 d ($C^{3,5}$, C_6H_4, $^2J_{CF}$ = 23.6 Hz), 121.6 t ($C^{2,6}$, C_6H_4, $^3J_{CF} \approx {}^3J_{CP}$ = 7.5 Hz), 123.3 q (CF_3, $^1J_{CF}$ = 278.3 Hz), 147.1 (C^1, C_6H_4), 159.7 d (C^4, C_6H_4, $^1J_{CF}$ = 243.4 Hz). ^{19}F NMR spectrum, δ_F, ppm: –118.6 q (FC_6H_4, $^3J_{FH} \approx {}^4J_{FH}$ = 6.1 Hz), –75.2 t. d (CF_3, $^3J_{FH}$ = 8.0, $^4J_{FP}$ = 4.0 Hz). ^{31}P NMR spectrum: δ_P 133.5 ppm. Found, %: C 35.08; H 2.31; F 39.13; P 8.90. $C_{10}H_8F_7O_3P$. Calculated, %: C 35.31; H 2.37; F 39.10; P 9.11.

Symmetrization of phosphites 6c and 6d. Phosphite **6c** or **6d** (1 g) was placed in an ampoule, which was filled with argon and then kept for 14 days. The reaction mixture was analyzed with the ^{1}H and ^{31}P NMR spectroscopy methods. In the spectra, along with the signals of non-symmetric phosphites **6c** and **6d**, there are the signals of symmetric phosphites **7**–**9** (identified using authentic samples). The ratio of compounds was **6c** : **7** : **8** = 24 : 1 : 0.5 and **6d** : **7** : **9** = 24 : 2 : 1. The spectral characteristics of compounds **7**–**9** are identical to published data [34, 35].

Tris(2,2,2-trifluoroethyl) phosphite (7). ^{31}P NMR spectrum ($CDCl_3$): δ_P 139.2 ppm (δ_P 139.3 ppm [34]).

Tris(4-methoxyphenyl) phosphite (8). ^{31}P NMR spectrum ($CDCl_3$): δ_P 127.5 ppm (δ_P 128.9 ppm [35]).

Tris(4-fluorophenyl) phosphite (9). ^{31}P NMR spectrum ($CDCl_3$): δ_P 127.7 ppm (δ_P 127.5 ppm [35]).

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CONFLICT OF INTEREST

No conflict of interest was declared by the authors.

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