ISSN 1070-3632, Russian Journal of General Chemistry, 2018, Vol. 88, No. 4, pp. 705–712. © Pleiades Publishing, Ltd., 2018.
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Synthesis and Isomer Composition of 2-Polyfluoroalkoxy-1,3,2-dioxaphospholanes and -phosphinanes

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Received November 9, 2017

Abstract—Polyfluoroalkanols readily reacted with 2-chloro-1,3,2-dioxaphospholanes and 2-chloro-1,3,2-dioxaphosphinanes in hexane in the presence of triethylamine (–10 to 25°C, 5 h) to give 2-polyfluoroalkoxy-1,3,2-dioxaphospholanes and 2-polyfluoroalkoxy-1,3,2-dioxaphosphinanes in 48–72% yield. The products were found to exist as mixtures of *cis* and *trans* isomers with the *trans* isomer predominating for the phospholanes and *cis* isomer predominating for the phosphinanes according to the ^{1}H, ^{13}C, ^{19}F, and ^{31}P NMR data.

Keywords: 2-chloro-1,3,2-dioxaphospholanes, 2-chloro-1,3,2-dioxaphosphinanes, polyfluoroalkanols, 2-polyfluoroalkoxy-1,3,2-dioxaphospholanes, 2-polyfluoroalkoxy-1,3,2-dioxaphosphinanes

DOI: 10.1134/S107036321804014X

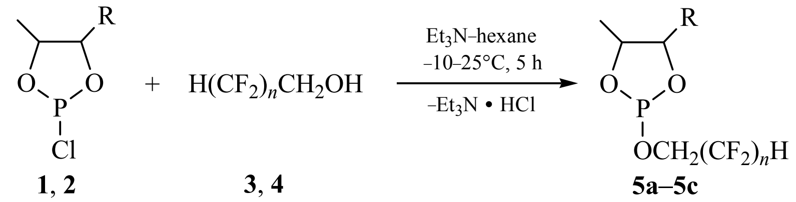
1,3,2-Dioxaphospholanes and 1,3,2-dioxaphosphinanes possessing a three-coordinate phosphorus atom are continuously used as promising intermediate products for the design of medicinal agents [1–4], efficient ligands for the preparation of metal complex catalysts [5–7], fire retardants for the protection of polymeric materials [8–10], building blocks for organometallic synthesis [11–17], and models for structural studies [18–21]. In recent time, particular attention has been given to directed synthesis of fluorinated phospholanes and phosphinanes that are needed as incombustible and oxidative additives to electrolytes [22–24]. Furthermore, the presence of pharmacophoric fluoroalkyl groups [25, 26] in phosphorus-containing heterocycles suggests enhanced pharmacological activity of these compounds.

The goal of the present work was to synthesize new 2-polyfluoroalkoxy-1,3,2-dioxaphospholanes and 2-polyfluoroalkoxy-1,3,2-dioxaphosphinanes and study in detail their isomer composition.

2-Polyfluoroalkoxy-1,3,2-dioxaphospholanes **5a**–**5c** were synthesized in 48–63% yields by reaction of 2-chloro-1,3,2-dioxaphospholanes **1** and **2** with polyfluoroalkanols **3** and **4** in the system triethylamine–hexane under mild conditions (–10 to 25°C, 5 h; Scheme 1). Under analogous conditions, 2-chloro-1,3,2-dioxaphosphinanes **6** and **7** reacted with polyfluorinated alcohols **3** and **4** to afford 48–72% of 2-polyfluoroalkoxy-1,3,2-dioxaphosphinanes **8a**–**8c** (Scheme 2). 2-Polyfluoroalkoxy-1,3,2-dioxaphosphinanes **8d** and **8e** were also obtained according to a two-step procedure including initial preparation of 2,2,3,3,4,4,5,5-octafluoropentyl phosphorodichloridite (**9**) and subsequent reaction of the latter with alkane-1,3-diols **10a** and **10b** (pyridine–diethyl ether, –10 to 25°C, 5 h). Compounds **8d** and **8e** were isolated in 45 and 53% yield, respectively (Scheme 3).

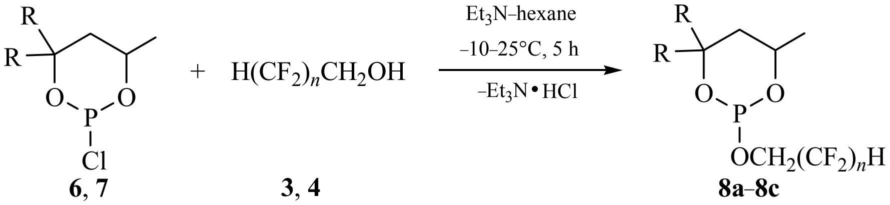
The isomer composition of phospholanes **5** and phosphinanes **8** was studied by ^{1}H, ^{13}C, ^{19}F, and ^{31}P NMR spectroscopy, including two-dimensional homo-

Scheme 1.



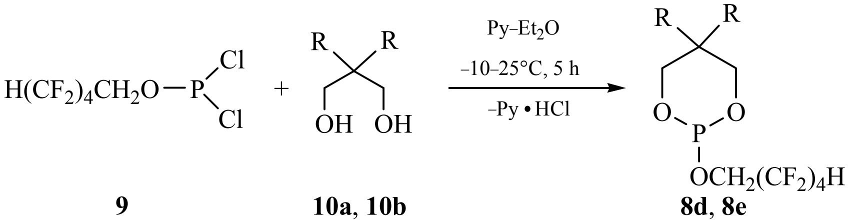
R = H (**1**, **5a**, **5b**), Me (**2**, **5c**); *n* = 2 (**3**, **5a**), 4 (**4**, **5b**, **5c**).

Scheme 2.



R = H (**6**, **8a**, **8b**), Me (**7**, **8c**); *n* = 2 (**3**, **8a**), 4 (**4**, **8b**, **8c**).

Scheme 3.

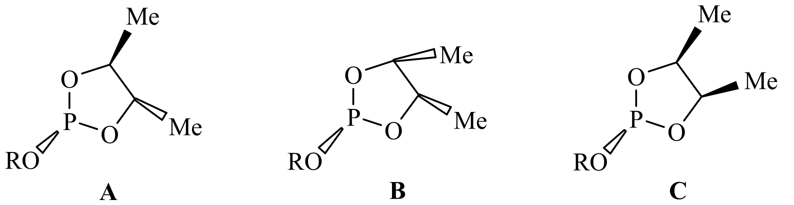


R = H (**8d**, **10a**), Me (**8e**, **10b**).

and heteronuclear shift correlation techniques (COSY, HSQC, HMBC). According to the ^{1}H, ^{13}C, and ^{31}P NMR data, phospholanes **5a** and **5b** containing one methyl group on the heterocycle exist as mixtures of two isomers with *cis* and *trans* orientations of the alkoxy group on the phosphorus atom and methyl group on C^4. The *cis*/*trans* isomer ratio was estimated at 1 : 1.5, which reflected higher thermodynamic stability of the *trans* isomer [27]. 4,5-Dimethyl-1,3,2-phospholane **5c** was found to exist as a mixture of three isomers (Scheme 4). The major isomer (**A**, *R*,*R*/*S*,*S* enantiomer pair) is characterized by *trans* orientation of the two methyl groups, while the methyl groups in the other two isomers, **B** and **C** (*meso* forms), are oriented *cis* with respect to each other. The methyl groups in **B** (*R*,*S*-*cis*, second abundant isomer) are oriented *cis* with respect to the fluoroalkoxy substituent, and the fluoroalkoxy group in **C** (*R*,*S*-*trans*, minor isomer) appears in *trans* orientation with respect to both methyl groups. The isomer ratio **A** : **B** : **C** is 7 : 2 : 1.

A considerably higher fraction of isomer **A** is likely to be determined by higher thermodynamic stability of the structure with *trans* orientation of the methyl groups on C^4 and C^5. The isomers were identified on the basis of differences in their ^{1}H, ^{13}C, and ^{31}P NMR spectra [27, 28]. The phosphorus nucleus in the 2,4-*trans* isomers of **5a** and **5b** resonated in the ^{31}P NMR spectra in a stronger field (by 3–4 ppm) relative to the corresponding signal of their *cis* isomers. The ^{31}P signal of the *R*,*S*-*trans* isomer (**C**) is located in a stronger field (δ_P 136–139 ppm) relative to those of the *R*,*R*/*S*,*S* and *R*,*S*-*cis* isomers (**A** and **B**; δ_P 140–144 and 148–150 ppm, respectively). Protons of the methyl groups oriented *trans* with respect to the substituent on the phosphorus atom resonated 0.1 ppm upfield from those of the *cis*-methyl groups. The 4-H and 5-H signals of the *trans* isomer were located in a weaker field ($\Delta\delta$ = 0.3–0.4 ppm). The vicinal coupling constant $^{3}J_{PC}$ between the phosphorus nucleus and methyl carbon nucleus in the *trans* position with

Scheme 4.



respect to the fluoroalkoxy group is 3–6 Hz against ~1 Hz for the *cis*-methyl group.

Phosphinanes **8a**–**8c** were mixtures of two isomers with *cis* and *trans* arrangements of the fluoroalkoxy substituent on the phosphorus atom and methyl group on C^4 (C^6), the *cis* isomer prevailing. The isomers were identified on the basis of NMR data [29–31]. The ^{31}P signals of the *trans* isomers (axial orientation of the substituent on the phosphorus atom) appeared in a stronger field (by 4 ppm). The vicinal coupling constant $^3J_{PC}$ for the *cis* isomers was considerably higher (12–16 Hz) than for the *trans* isomers ($^3J_{PC}$ = 5 Hz) [31, 32].

It is known that unlike carbon analogs, 1,3-dioxanes, 2-substituted 1,3,2-dioxaphosphinanes prefer axial orientation of the substituent on the phosphorus atom [27, 32]. This is related to more favorable vicinal interaction between lone electron pairs on the oxygen atoms and vacant anti-bonding orbital of the P–X bond. The fact that the major isomers of **8a**–**8c** are *cis* with equatorial orientation of the substituent on the phosphorus atom is likely to be determined by the length of the fluoroalkoxy group and kinetic control of the reaction. The latter assumption was confirmed by slow isomerization of **8a** (with a relatively short 2-substituent) in $CDCl_3$ solution: the initial *cis*/*trans* ratio (8:1) changed to 1:1.3 in several days. Analogous isomerization was observed previously [32].

Thus, convenient procedures have been developed for the synthesis of new 2-polyfluoroalkoxy-1,3,2-dioxaphospholanes and 2-polyfluoroalkoxy-1,3,2-dioxaphosphinanes from accessible alkanediols, fluorinated alcohols, and phosphorus trichloride, and isomer compositions of the isolated compounds have been studied in detail.

EXPERIMENTAL

The ^1H, ^{13}C, ^{19}F, and ^{31}P NMR spectra were recorded on Bruker DPX 400 and Bruker AV-400 spectrometers (400.13, 101.61, 376.50, and 161.98 MHz, respectively) from solutions in $CDCl_3$; the chemical shifts were measured relative to hexamethyldisiloxane (^1H, ^{13}C; internal standard), $CFCl_3$ (^{19}F, internal standard), or 85% H_3PO_4 (^{31}P, external standard). Signals in the ^1H and ^{13}C NMR spectra were assigned using two-dimensional homo- and heteronuclear shift correlation techniques (COSY, HSQC, HMBC). The IR spectra were recorded from thin films on a Bruker IFS 25 spectrometer.

Initial 2-chloro-1,3,2-dioxaphospholanes **1** and **2** and 2-chloro-1,3,2-dioxaphosphinanes **6** and **7** were synthesized from phosphorus trichloride and the corresponding diols [33]. 2,2,3,3,4,4,5,5-Octafluoropentyl phosphorodichloridite (**9**) was synthesized from phosphorus trichloride as described in [34].

General procedure for the synthesis of 1,3,2-dioxaphospholanes 5a–5c and 1,3,2-dioxaphosphinanes 8a–8c. A solution of 2-chloro-1,3,2-dioxaphospholane **1** or **2** or 2-chloro-1,3,2-dioxaphosphinane **6** or **7** in 10 mL of hexane was added dropwise with stirring over a period of 2 h to a solution of 0.05 mol of polyfluoroalkanol **3** or **4** and 6.1 g (0.06 mol) of triethylamine in 80 mL of hexane, maintaining the temperature at –10 to –5°C. Triethylamine hydrochloride separated from the solution as a white solid. The cooling bath was removed, and the mixture was stirred for 3 h at room temperature and left overnight. The precipitate was filtered off and washed with hexane (3×20 mL). The filtrate was combined with the washings, the solvent was distilled off under reduced pressure, and the residue was distilled in a vacuum.

4-Methyl-2-(2,2,3,3-tetrafluoropropoxy)-1,3,2-dioxaphospholane (5a). Yield 6.3 g (53%, *cis*/*trans* ratio 1:1.5), colorless liquid, bp 93–94°C (24 mm). IR spectrum, ν, cm^{-1}: 2984 s, 2936 m, 2901 m, 1457 m, 1385 m, 1303 m, 1289 m, 1231 s, 1207 s, 1127 s, 1107 s, 1076 s, 1066 s, 989 s, 938 m, 916 m, 864 s, 833 s, 785 s, 750 s, 668 m, 622 m, 544 s, 484 m. ^1H NMR spectrum, δ, ppm: *trans* isomer: 1.33 d (3H, CH_3, $^3J_{HH}$ = 6.2 Hz), 3.57 t.d (1H, 5-H, $^2J_{HH}$ = 8.3, $^3J_{HH}$ = $^3J_{PH}$ =

7.4 Hz), 4.16 d.d.t and 4.07 d.d.t (2H, $\mathrm{CH_2CF_2}$, $^2J_{\mathrm{HH}}$ = 6.0, $^3J_{\mathrm{HF}}$ = 1.5, $^3J_{\mathrm{HP}}$ = 12.4 Hz), 4.30 d.d.d (1H, 5-H, $^2J_{\mathrm{HH}}$ = 8.3, $^3J_{\mathrm{HH}}$ = 6.7, $^3J_{\mathrm{HP}}$ = 2.8 Hz), 4.59 d.d.q (1H, 4-H, $^3J_{\mathrm{HH}}$ = 7.4, $^3J_{\mathrm{HH}}$ = 6.7, 6.2 Hz), 5.88 t.t (1H, $\mathrm{CHF_2}$, $^2J_{\mathrm{HF}}$ = 53.2, $^3J_{\mathrm{HF}}$ = 4.7 Hz); *cis* isomer: 1.44 d (3H, $\mathrm{CH_3}$, $^3J_{\mathrm{HH}}$ = 6.2 Hz), 3.70 t (1H, 5-H, $^2J_{\mathrm{HH}}$ = $^3J_{\mathrm{HH}}$ = 8.9 Hz), 4.16 d.d.t and 4.07 d.d.t (2H, $\mathrm{CH_2CF_2}$, $^2J_{\mathrm{HH}}$ = 6.0, $^3J_{\mathrm{HF}}$ = 1.5, $^3J_{\mathrm{HP}}$ = 12.4 Hz), 4.21 d.d.d (1H, 5-H, $^2J_{\mathrm{HH}}$ = 8.9, $^3J_{\mathrm{HH}}$ = 6.5, $^3J_{\mathrm{HP}}$ = 13.2 Hz), 4.34 m (1H, CH), 5.88 t.t (1H, $\mathrm{CHF_2}$, $^2J_{\mathrm{HF}}$ = 53.2, $^3J_{\mathrm{HF}}$ = 4.7 Hz). ^{19}F NMR spectrum, δ_{F}, ppm: *trans* isomer: –139.6 d ($\mathrm{CHF_2}$, $^2J_{\mathrm{FH}}$ = 53.2 Hz), –125.9 m ($\mathrm{CF_2}$); *cis* isomer: –139.4 d ($\mathrm{CHF_2}$, $^2J_{\mathrm{FH}}$ = 53.2 Hz), –125.8 m ($\mathrm{CF_2}$). ^{31}P NMR spectrum, δ_{P}, ppm: 140.3 (*trans*), 143.7 (*cis*). Found, %: C 30.12; H 4.13; P 12.63. $\mathrm{C_6H_9F_4O_3P}$. Calculated, %: C 30.52; H 3.84; P 13.12.

4-Methyl-2-(2,2,3,3,4,4,5,5-octafluoropentyloxy)-1,3,2-dioxaphospholane (5b). Yield 8.1 g (48%, *cis*/*trans* ratio 1:1.5), transparent liquid, bp 106–108°C (17 mm), d_4^{20} = 1.5240, n_{D}^{20} = 1.3712. IR spectrum, ν, cm^{-1}: 2985 s, 2939 m, 2904 m, 1475 w, 1458 s, 1402 m, 1386 s, 1360 m, 1291 s, 1266 m, 1243 m, 1223 m, 1204 m, 1172 s, 1131 s, 1093 m, 1070 m, 1046 m, 1014 m, 990 s, 961 m, 944 m, 902 s, 864 s, 808 s, 772 s, 754 s, 733 m, 713 m, 689 m, 675 w, 620 m, 607 m, 573 w, 560 w, 545 m, 520 w, 492 m. ^{1}H NMR spectrum, δ, ppm: *trans* isomer: 1.33 d (3H, $\mathrm{CH_3}$, $^3J_{\mathrm{HH}}$ = 6.2 Hz), 3.57 d.d.d (1H, 5-H, $^2J_{\mathrm{HH}}$ = 8.5, $^3J_{\mathrm{HH}}$ = 7.1, $^3J_{\mathrm{HP}}$ = 7.7 Hz), 4.19 m (2H, $\mathrm{CH_2CF_2}$), 4.30 d.d.d (1H, 5-H, $^2J_{\mathrm{HH}}$ = 8.5, $^3J_{\mathrm{HH}}$ = 6.6, $^3J_{\mathrm{PH}}$ = 2.7 Hz), 4.61 d.d.q (1H, 4-H, $^3J_{\mathrm{HH}}$ = 7.1, $^3J_{\mathrm{HH}}$ = 6.6, 6.2 Hz), 6.047 t.t (1H, $\mathrm{CHF_2}$, $^2J_{\mathrm{HF}}$ = 52.1, $^3J_{\mathrm{HF}}$ = 5.4 Hz); *cis* isomer: 1.44 d (3H, $\mathrm{CH_3}$, $^3J_{\mathrm{HH}}$ = 6.2 Hz), 3.72 d.d (1H, 5-H, $^2J_{\mathrm{HH}}$ = $^3J_{\mathrm{HH}}$ = 8.9 Hz), 4.19 m (2H, $\mathrm{CH_2CF_2}$), 4.22 m (1H, 5-H), 4.34 m (1H, 4-H), 6.051 t.t (1H, $\mathrm{CHF_2}$, $^2J_{\mathrm{HF}}$ = 52.0, $^3J_{\mathrm{HF}}$ = 5.5 Hz). ^{13}C NMR spectrum, δ_{C}, ppm: *trans* isomer: 19.5 d ($\mathrm{CH_3}$, $^3J_{\mathrm{CP}}$ = 4.0 Hz), 59.7 t.d ($\mathrm{CH_2CF_2}$, $^2J_{\mathrm{CF}}$ = 26.4, $^2J_{\mathrm{CP}}$ = 17.2 Hz), 70.4 d ($\mathrm{C^5}$, $^2J_{\mathrm{CP}}$ = 7.7 Hz), 72.7 d ($\mathrm{C^4}$, $^2J_{\mathrm{CP}}$ = 8.1 Hz), 107.7 t.t ($\mathrm{HCF_2}$, $^1J_{\mathrm{CF}}$ = 254.6, $^2J_{\mathrm{CF}}$ = 30.8 Hz), 110.2 t.q ($\mathbf{C}\mathrm{F_2CHF_2}$, $^1J_{\mathrm{CF}}$ = 264.5, $^2J_{\mathrm{CF}}$ = 31.3 Hz), 111.0 t.q ($\mathbf{C}\mathrm{F_2CF_2CH_2}$, $^1J_{\mathrm{CF}}$ = 264.8, $^2J_{\mathrm{CF}}$ = 33.0 Hz), 114.9 t.t.d ($\mathbf{C}\mathrm{F_2CH_2}$, $^1J_{\mathrm{CF}}$ = 255.7, $^2J_{\mathrm{CF}}$ = 30.5, $^3J_{\mathrm{CP}}$ = 3.7 Hz); *cis* isomer: 19.6 ($\mathrm{CH_3}$), 59.8 t.d ($\mathrm{CH_2CF_2}$, $^2J_{\mathrm{CF}}$ = 26.8, $^2J_{\mathrm{CP}}$ = 18.7 Hz), 69.7 d ($\mathrm{C^5}$, $^2J_{\mathrm{CP}}$ = 7.3 Hz), 74.8 d ($\mathrm{C^4}$, $^2J_{\mathrm{CP}}$ = 9.5 Hz), 107.7 t.t ($\mathrm{CHF_2}$, $^1J_{\mathrm{CF}}$ = 254.6, $^2J_{\mathrm{CF}}$ = 30.8 Hz), 110.2 t.q ($\mathbf{C}\mathrm{F_2CHF_2}$, $^1J_{\mathrm{CF}}$ = 264.5, $^2J_{\mathrm{CF}}$ = 31.3 Hz), 111.0 t.q ($\mathbf{C}\mathrm{F_2CF_2CH_2}$, $^1J_{\mathrm{CF}}$ = 264.8, $^2J_{\mathrm{CF}}$ = 33.0 Hz), 114.9 t.t.d ($\mathbf{C}\mathrm{F_2CH_2}$, $^1J_{\mathrm{CF}}$ = 255.7, $^2J_{\mathrm{CF}}$ = 30.5, $^3J_{\mathrm{CP}}$ = 3.7 Hz). ^{19}F NMR spectrum, δ_{F}, ppm: –137.5 d ($\mathrm{CHF_2}$, $^2J_{\mathrm{FH}}$ = 52.0 Hz), –130.4 m ($\mathrm{C}\mathbf{F}_2\mathrm{CHF_2}$), –125.4 m ($\mathrm{C}\mathbf{F}_2\mathrm{CF_2CHF_2}$), –120.5 m ($\mathrm{CH_2CF_2}$). ^{31}P NMR spectrum, δ_{P}, ppm: 142.0 t ($^4J_{\mathrm{PF}}$ = 6.9 Hz, *trans*), 145.1 t ($^4J_{\mathrm{PF}}$ = 6.9 Hz, *cis*). Found, %: C 28.30; H 2.58; F 44.94; P 8.92. $\mathrm{C_8H_9F_8O_3P}$. Calculated, %: C 28.59; H 2.70; F 45.22; P 9.22.

4,5-Dimethyl-2-(2,2,3,3,4,4,5,5-octafluoropentyloxy)-1,3,2-dioxaphospholane (5c). Yield 11.0 g (63%, isomer ratio 7:2:1), transparent liquid, bp 115–116°C (10 mm), d_4^{20} = 1.4917, n_{D}^{20} = 1.3765. IR spectrum, ν, cm^{-1}: 2986 s, 2937 s, 1457 s, 1445 s, 1386 s, 1332 m, 1302 m, 1289 s, 1264 m, 1244 m, 1173 s, 1132 s, 1093 s, 1076 s, 1060 s, 1043 s, 1020 m, 993 m, 960 m, 932 s, 900 m, 870 m, 855 m, 808 m, 785 s, 767 s, 713 m, 689 w, 674 w, 618 m, 545 m, 525 w, 471 w, 457 w, 438 m. ^{1}H NMR spectrum, δ, ppm: *R*,*R*/*S*,*S* isomer: 1.32 d (3H, $\mathrm{CH_3}$, $^3J_{\mathrm{HH}}$ = 6.0 Hz), 1.38 d (3H, $\mathrm{CH_3}$, $^3J_{\mathrm{HH}}$ = 6.0 Hz), 3.78 d.q.d (1H, CH, $^3J_{\mathrm{HH}}$ = 8.5, 6.0, $^3J_{\mathrm{HP}}$ = 3.8 Hz), 4.04 d.q (1H, CH, $^3J_{\mathrm{HH}}$ = 8.5, 6.0 Hz), 4.19 t.d (2H, $\mathrm{CH_2}$, $^3J_{\mathrm{HF}}$ = 13.8, $^3J_{\mathrm{HP}}$ = 8.4 Hz), 6.03 t.t (1H, $\mathrm{CHF_2}$ $^1J_{\mathrm{HF}}$ = 52.0, $^3J_{\mathrm{HF}}$ = 5.4 Hz); *R*,*S*-*cis* isomer: 1.32 d (6H, $\mathrm{CH_3}$, $^3J_{\mathrm{HH}}$ = 6.0 Hz), 4.22 t.d (2H, $\mathrm{CH_2}$, $^3J_{\mathrm{HF}}$ = 13.8, $^3J_{\mathrm{HP}}$ = 8.4 Hz), 4.38 q.d.d (2H, CH, $^3J_{\mathrm{HH}}$ = 6.0, 2.0, $^3J_{\mathrm{HP}}$ = 4.5 Hz), 6.03 t.t (1H, $\mathrm{CHF_2}$, $^1J_{\mathrm{HF}}$ = 52.0, $^3J_{\mathrm{HF}}$ = 5.4 Hz); *R*,*S*-*trans* isomer: 1.19 d (6H, $\mathrm{CH_3}$, $^3J_{\mathrm{HH}}$ = 6.0 Hz), 4.53 m (2H, CH), 6.03 t.t (1H, $\mathrm{CHF_2}$, $^1J_{\mathrm{HF}}$ = 52.0, $^3J_{\mathrm{HF}}$ = 5.4 Hz); signals of the $\mathrm{CH_2}$ protons were overlapped by more intense signals of the other isomers. ^{13}C NMR spectrum, δ_{C}, ppm: *R*,*R*/*S*,*S* isomer: 17.9 d ($\mathrm{CH_3}$, $^3J_{\mathrm{CP}}$ = 5.5 Hz), 18.8 ($\mathrm{CH_3}$), 59.6 t.d ($\mathrm{CH_2}$, $^2J_{\mathrm{CF}}$ = 26.5, $^2J_{\mathrm{CP}}$ = 19.5 Hz), 78.5 d (CH, $^2J_{\mathrm{CP}}$ = 7.4 Hz), 80.7 d (CH, $^2J_{\mathrm{CP}}$ = 8.1 Hz), 107.5 t.t ($\mathrm{CHF_2}$, $^1J_{\mathrm{CF}}$ = 254.0, $^2J_{\mathrm{CF}}$ = 31.0 Hz), 110.0 t.q ($\mathbf{C}\mathrm{F_2CHF_2}$, $^1J_{\mathrm{CF}}$ = 264.3, $^2J_{\mathrm{CF}}$ = 31.0 Hz), 110.8 t.q ($\mathbf{C}\mathrm{F_2CF_2CH_2}$, $^1J_{\mathrm{CF}}$ = 265.0, $^2J_{\mathrm{CF}}$ = 31.3 Hz), 114.7 t.t.d ($\mathbf{C}\mathrm{F_2CH_2}$, $^1J_{\mathrm{CF}}$ = 256.2, $^2J_{\mathrm{CF}}$ = 30.6, $^3J_{\mathrm{CP}}$ = 4.1 Hz); *R*,*S*-*cis* isomer: 16.5 ($\mathrm{CH_3}$), 59.5 t.d ($\mathrm{CH_2}$, $^2J_{\mathrm{CF}}$ = 26.5, $^2J_{\mathrm{CP}}$ = 18.4 Hz), 76.4 d (CH, $^2J_{\mathrm{CP}}$ = 8.5 Hz), 107.5 t.t ($\mathrm{CHF_2}$, $^1J_{\mathrm{CF}}$ = 254.0, $^2J_{\mathrm{CF}}$ = 31.0 Hz), 110.0 t.q ($\mathbf{C}\mathrm{F_2CHF_2}$, $^1J_{\mathrm{CF}}$ = 264.3, $^2J_{\mathrm{CF}}$ = 31.0 Hz), 110.8 t.q ($\mathbf{C}\mathrm{F_2CF_2CH_2}$, $^1J_{\mathrm{CF}}$ = 265.0, $^2J_{\mathrm{CF}}$ = 31.3 Hz), 114.7 t.t.d ($\mathbf{C}\mathrm{F_2CH_2}$, $^1J_{\mathrm{CF}}$ = 256.2, $^2J_{\mathrm{CF}}$ = 30.6, $^3J_{\mathrm{CP}}$ = 4.1 Hz); *R*,*S*-*trans* isomer: 15.7 d ($\mathrm{CH_3}$, $^3J_{\mathrm{CP}}$ = 3.3 Hz), 74.8 d (CH, $^2J_{\mathrm{CP}}$ = 7.4 Hz), 107.5 t.t ($\mathrm{CHF_2}$, $^1J_{\mathrm{CF}}$ = 254.0, $^2J_{\mathrm{CF}}$ = 31.0 Hz), 110.0 t.q ($\mathbf{C}\mathrm{F_2CHF_2}$, $^1J_{\mathrm{CF}}$ = 264.3, $^2J_{\mathrm{CF}}$ = 31.0 Hz), 110.8 t.q ($\mathbf{C}\mathrm{F_2CF_2CH_2}$, $^1J_{\mathrm{CF}}$ = 265.0, $^2J_{\mathrm{CF}}$ = 31.3 Hz), 114.7 t.t.d ($\mathbf{C}\mathrm{F_2CH_2}$, $^1J_{\mathrm{CF}}$ = 256.2, $^2J_{\mathrm{CF}}$ = 30.6, $^3J_{\mathrm{CP}}$ = 4.1 Hz); the $\mathrm{CH_2}$ multiplet was overlapped by more intense signals of the other isomers. ^{19}F NMR spectrum, δ_{F}, ppm: –137.4 d ($\mathrm{CHF_2}$, $^1J_{\mathrm{FH}}$ = 52.0), –130.4 m ($\mathrm{C}\mathbf{F}_2\mathrm{CHF_2}$),

–125.4 m ($C\mathbf{F}_2CF_2CHF_2$), –120.4 m (CH_2CF_2). ^{31}P NMR spectrum, δ_P, ppm: 139.5 t ($^4J_{PF}$ = 7.2 Hz, *R*,*S*-*trans*), 144.1 t ($^4J_{PF}$ = 6.9 Hz, *R*,*R*/*S*,*S*), 149.7 ($^4J_{PF}$ = 8.6 Hz, *R*,*S*-*cis*). Found, %: C 30.64; H 2.92; F 43.36; P 8.58. $C_9H_{11}F_8O_3P$. Calculated, %: C 30.87; H 3.17; F 43.41; P 8.85.

4-Methyl-2-(2,2,3,3-tetrafluoropropoxy)-1,3,2-dioxaphosphinane (8a). Yield 9.0 g (72%, *cis*/*trans* ratio 8:1), transparent liquid, bp 67°C (1 mm), d_4^{20} = 1.2936, n_D^{20} = 1.4039. IR spectrum, ν, cm^{-1}: 2980 s, 2937 s, 2904 m, 1476 m, 1457 m, 1413 w, 1386 s, 1351 w, 1337 w, 1253 s, 1233 s, 1209 m, 1106 s, 1066 s, 1034 s, 1005 m, 981 m, 966 m, 923 s, 886 m, 832 m, 748 s, 668 m, 653 w, 611 w, 583 w, 547 m, 523 m, 501 w, 487 w, 464 w, 398 w. ^1H NMR spectrum, δ, ppm: *cis* isomer (*eq*,*eq*): 1.40 d (3H, CH_3, $^3J_{HH}$ = 6.6 Hz), 1.96 d.d.d.d (1H, 5-H_{eq}, $^2J_{HH}$ = 14.9, $^3J_{\text{H-}eq\text{,H-}ax}$ = 10.8, 7.3, $^4J_{HP}$ = 4.0 Hz), 2.12 m (1H, 5-H_{ax}), 3.96 t.d.d (1H, 6-H_{ax}, $^2J_{HH}$ ≈ $^3J_{\text{H-}ax\text{,H-}ax}$ = 11.3, $^3J_{\text{H-}ax\text{,H-}eq}$ = 7.3, $^3J_{HP}$ = 4.2 Hz), 4.11 t.d (2H, CH_2CF_2, $^3J_{HF}$ = 12.6, $^3J_{HP}$ = 7.1 Hz), 4.31 m (1H, 6-H_{eq}), 4.34 m (1H, 4-H), 5.92 t.t (1H, CHF_2, $^2J_{HF}$ = 53.3, $^3J_{HF}$ = 4.4 Hz); *trans* isomer (*eq*,*ax*): 1.22 d (3H, CH_3, $^3J_{HH}$ = 6.3 Hz), 1.62 d.q (1H, 5-H_{eq}, $^2J_{HH}$ = 14.1, $^3J_{\text{H-}eq\text{,H-}eq}$ ≈ $^3J_{\text{H-}eq\text{,H-}eq}$ ≈ $^4J_{HP}$ ≈ $^3J_{\text{H-}eq\text{,H-}ax}$ ≈ 2.3 Hz), 2.08 m (1H, 5-H_{ax}), 3.83 t.d.d (1H, 6-H_{ax}, $^2J_{HH}$ ≈ $^3J_{\text{H-}ax\text{,H-}ax}$ = 10.7, $^3J_{\text{H-}ax\text{,H-}eq}$ = 4.5, $^3J_{HP}$ = 1.8 Hz), 4.11 t.d (2H, CH_2CF_2, $^3J_{HF}$ = 12.6, $^3J_{HP}$ = 7.1 Hz), 4.42 d.d.t (1H, 6-H_{eq}, $^2J_{HH}$ = 10.7, $^3J_{\text{H-}eq\text{,P}}$ = 13.1, $^3J_{\text{H-}eq\text{,H-}eq}$ ≈ $^3J_{\text{H-}eq\text{,H-}ax}$ = 2.3 Hz), 4.55 m (1H, 4-H), 5.93 t.t (1H, CHF_2, $^2J_{HF}$ = 53.3, $^3J_{HF}$ = 4.4 Hz). ^{13}C NMR spectrum, δ_C, ppm: *cis* isomer (*eq*,*eq*): 22.8 (CH_3), 32.8 d (C^5, $^3J_{CP}$ = 11.4 Hz), 58.8 d (C^6, $^2J_{CP}$ = 2.6 Hz), 59.6 t.d ($\mathbf{C}H_2CF_2$, $^2J_{CF}$ = 29.6, $^2J_{CP}$ = 18.7 Hz), 69.9 d (C^4, $^2J_{CP}$ = 4.9 Hz), 109.2 t.t (HCF_2, $^1J_{CF}$ = 249.5, $^2J_{CF}$ = 34.9 Hz), 114.8 t.t.d (CF_2, $^1J_{CF}$ = 253.3, $^2J_{CF}$ = 27.0, $^3J_{CP}$ = 6.5 Hz); *trans* isomer (*eq*,*ax*): 22.7 (CH_3), 35.4 d (C^5, $^3J_{CP}$ = 5.0 Hz), 60.0 t.d ($\mathbf{C}H_2CF_2$, $^2J_{CF}$ = 29.5, $^2J_{CP}$ = 19.9 Hz), 60.2 d (C^6, $^2J_{CP}$ = 2.6 Hz), 66.5 d (C^4, $^2J_{CP}$ = 2.1 Hz), 109.3 t.t (HCF_2, $^1J_{CF}$ = 249.7, $^2J_{CF}$ = 35.3 Hz), 114.8 t.t.d (CF_2, $^1J_{CF}$ = 250.0, $^2J_{CF}$ = 27.2, $^3J_{CP}$ = 6.5 Hz). ^{19}F NMR spectrum, δ_F, ppm: *cis* isomer (*eq*,*eq*): –138.9 d (CHF_2, $^2J_{FH}$ = 52.6 Hz), –125.4 m (CF_2); *trans* isomer (*eq*,*ax*): –139.1 d (CHF_2, $^2J_{FH}$ = 56.4 Hz), –125.6 m (CF_2). ^{31}P NMR spectrum, δ_P, ppm: 129.8 (*trans*), 133.6 (*cis*). Found, %: C 33.59; H 4.45; F 30.78; P 11.91. $C_7H_{11}F_4O_3P$. Calculated, %: C 33.61; H 4.43; F 30.38; P 12.38.

4-Methyl-2-(2,2,3,3,4,4,5,5-octafluoropentyloxy)-1,3,2-dioxaphosphinane (8b). Yield 12.6 g (72%, *cis*/*trans* ratio 18:1), transparent liquid, bp 98°C (2 mm), d_4^{20} = 1.4660, n_D^{20} = 1.3804. IR spectrum, ν, cm^{-1}: 2981 s, 2938 m, 2904 w, 1475 w, 1459 w, 1444 m, 1429 w, 1402 w, 1388 m, 1377 w, 1361 w, 1334 w, 1289 m, 1252 m, 1226 m, 1173 s, 1132 s, 1097 m, 1074 s, 1034 s, 982 m, 966 m, 925 s, 901 m, 887 m, 842 m, 809 m, 767 m, 752 s, 728 m, 629 w, 609 m, 573 w, 561 w, 546 m, 538 w, 520 w, 508 w, 487 w. ^1H NMR spectrum, δ, ppm: *cis* isomer (*eq*,*eq*): 1.39 d (3H, CH_3, $^3J_{HH}$ = 6.3 Hz), 2.04 d.d.d.d (1H, 5-H_{eq}, $^2J_{HH}$ = 14.3, $^3J_{\text{H-}eq\text{,H-}ax}$ = 10.8, $^3J_{\text{H-}eq\text{,H-}ax}$ = 7.3, $^4J_{HP}$ = 4.0 Hz), 2.15 m (1H, 5-H_{ax}), 3.97 t.t.d (1H, 6-H_{ax}, $^2J_{HH}$ ≈ $^3J_{\text{H-}ax\text{,H-}ax}$ = 11.3, $^3J_{\text{H-}ax\text{,H-}eq}$ = 7.7, $^3J_{HP}$ = 4.4 Hz), 4.25 t.d (2H, CH_2CF_2, $^3J_{HF}$ = 14.0, $^3J_{HP}$ = 7.5 Hz), 4.33 m (1H, 6-H_{eq}), 4.35 m (1H, 4-H), 6.04 t.t (1H, CHF_2, $^2J_{HF}$ = 52.0, $^3J_{HF}$ = 5.5 Hz); *trans* isomer (*eq*,*eq*): 1.20 d (3H, CH_3, $^3J_{HH}$ = 6.3 Hz), 1.61 d.q (1H, 5-H_{eq}, $^2J_{HH}$ = 14.3, $^3J_{\text{H-}eq\text{,H-}eq}$ ≈ $^3J_{\text{H-}eq\text{,H-}eq}$ ≈ $^4J_{HP}$ ≈ $^3J_{\text{H-}eq\text{,H-}ax}$ ≈ 2.2 Hz), 2.06 m (1H, 5-H_{ax}), 3.83 t.d.d (1H, 6-H_{ax}, $^2J_{HH}$ ≈ $^3J_{\text{H-}ax\text{,H-}ax}$ = 10.8, $^3J_{\text{H-}ax\text{,H-}eq}$ = 4.7, $^3J_{HP}$ = 1.9 Hz), 4.42 d.d.t (1H, 6-H_{eq}, $^2J_{HH}$ = 10.6, $^3J_{HP}$ = 13.0, $^3J_{\text{H-}eq\text{,H-}eq}$ ≈ $^3J_{\text{H-}eq\text{,H-}ax}$ = 2.1 Hz), 4.55 m (1H, 4-H), signals of the CH_2CF_2 and CHF_2 protons were overlapped by more intense signals of the *cis* isomer. ^{13}C NMR spectrum, δ_C, ppm: *cis* isomer (*eq*,*eq*): 22.7 (CH_3), 32.8 d (C^5, $^3J_{CP}$ = 11.8 Hz), 58.8 d (C^6, $^2J_{CP}$ = 2.6 Hz), 59.7 t.d ($\mathbf{C}H_2CF_2$, $^2J_{CF}$ = 26.5, $^2J_{CP}$ = 21.4 Hz), 70.1 d (C^4, $^2J_{CP}$ = 5.2 Hz), 107.7 t.t (HCF_2, $^1J_{CF}$ = 254.3, $^2J_{CF}$ = 30.6 Hz), 110.0 t.q ($HCF_2\mathbf{C}F_2$, $^1J_{CF}$ = 254.1, $^2J_{CF}$ = 30.5 Hz), 111.0 t.q ($\mathbf{C}F_2CF_2CH_2$, $^1J_{CF}$ = 265.0, $^2J_{CF}$ = 30.2 Hz), 115.2 t.t.d ($\mathbf{C}F_2CH_2$, $^1J_{CF}$ = 256.9, $^2J_{CF}$ = 30.6, $^3J_{CP}$ = 5.5 Hz); *trans* isomer (*eq*,*ax*): 21.2 d (CH_3, $^3J_{CP}$ = 4.9 Hz), 35.4 d (C^5, $^3J_{CP}$ = 4.8 Hz), 60.3 d (C^6, $^2J_{CP}$ = 2.0 Hz), 66.6 (C^4); signals of the $H(CF_2)_4CH_2$ fragment were overlapped by more intense signals of the *cis* isomer. ^{19}F NMR spectrum, δ_F, ppm: *cis* isomer (*eq*,*eq*): –137.5 d.m (CHF_2, $^2J_{FH}$ = 52.0 Hz), –130.4 m ($C\mathbf{F}_2CHF_2$), –125.4 m ($C\mathbf{F}_2CF_2CHF_2$), –120.5 m (CH_2CF_2). ^{31}P NMR spectrum, δ_P, ppm: 130.7 t ($^4J_{PF}$ = 5.7 Hz, *trans*), 134.2 t ($^4J_{PF}$ = 5.7 Hz, *cis*). Found, %: C 30.61; H 3.16; F 43.62; P 9.12. $C_9H_{11}F_8O_3P$. Calculated, %: C 30.87; H 3.17; F 43.41; P 8.85.

4,4,6-Trimethyl-2-(2,2,3,3,4,4,5,5-octafluoropentyloxy)-1,3,2-dioxaphosphinane (8c). Yield 9.14 g (48%, *cis*/*trans* ratio 2:1), transparent liquid, bp 78–79°C (1 mm), d_4^{20} = 1.4029, n_D^{20} = 1.3874. IR spectrum, ν, cm^{-1}: 2982 s, 2938 s, 2880 m, 2832 m, 1459 m, 1383 s, 1374 s, 1336 m, 1307 s, 1289 s, 1281 s, 1245 m, 1229 m, 1206 m, 1173 s, 1132 s, 1089 s, 1045 s, 979 s, 963 s, 934 s, 901 s, 879 m, 827 m, 809 s, 764 s, 752 s, 726 m, 707 m, 688 w, 629 w, 606 m, 574 w, 563 w, 546 m, 538 w, 520 m, 478 w, 458 w, 393 w, 379 w. ^{1}H NMR spectrum, δ, ppm: *cis* isomer (*eq*,*eq*): 1.29 d (3H, 6-CH_3, $^3J_{\text{HH}}$ = 6.0 Hz), 1.35 s and 1.39 s (3H each, 4-CH_3), 1.68 d.d.d (1H, 5-H_{eq}, $^2J_{\text{HH}}$ = 14.5, $^3J_{\text{H-}eq\text{,H-}ax}$ = $^4J_{\text{HP}}$ = 3.4 Hz), 2.44 d.d (1H, 5-H_{ax}, $^2J_{\text{HH}}$ = 14.5, $^3J_{\text{H=}ax\text{,H-}ax}$ = 13.1 Hz), 4.20 t.d (2H, CH_2CF_2, $^3J_{\text{HF}}$ = 13.6, $^3J_{\text{HP}}$ = 7.0 Hz), 4.36 d.q.d.d. (1H, 6-H_{ax}, $^3J_{\text{H-}ax\text{,H-}ax}$ = 13.1, $^3J_{\text{H-}ax\text{,CH3}}$ = 6.0, $^3J_{\text{H-}ax\text{,H-}eq}$ = 3.4, $^3J_{\text{HP}}$ = 2.8 Hz), 6.06 t.t (1H, CHF_2, $^2J_{\text{HF}}$ = 52.0, $^3J_{\text{HF}}$ = 4.7 Hz); *trans* isomer (*eq*,*ax*): 1.25 d (3H, 6-CH_3, $^3J_{\text{HH}}$ = 6.2 Hz), 1.29 s and 1.50 s (3H each, 4-CH_3), 1.63 d.d.d (1H, 5-H_{eq}, $^2J_{\text{HH}}$ = 13.9, $^3J_{\text{H-}eq\text{,H-}ax}$ = 3.2, $^4J_{\text{HP}}$ = 2.0 Hz), 1.84 d.d (1H, 5-H_{ax}, $^2J_{\text{HH}}$ = 13.9, $^3J_{\text{H-}ax\text{,H-}ax}$ = 11.6 Hz), 4.19 t.d (2H, CH_2CF_2, $^3J_{\text{HF}}$ = 14.2, $^3J_{\text{HP}}$ = 7.2 Hz), 4.62 d.q.d.d (1H, 6-H_{ax}, $^3J_{\text{H-}ax\text{,H-}ax}$ = 11.6, $^3J_{\text{H-}ax\text{,CH3}}$ = 6.2, $^3J_{\text{H-}ax\text{,H-}eq}$ = 3.2, $^3J_{\text{HP}}$ = 2.8 Hz), 6.06 t.t (1H, CHF_2, $^2J_{\text{HF}}$ = 52.0, $^3J_{\text{HF}}$ = 5.6 Hz). ^{13}C NMR spectrum, δ_C, ppm: *cis* isomer (*eq*,*eq*): 23.6 (6-CH_3), 28.2 d (4-CH_3, *ax*, $^3J_{\text{CP}}$ = 1.5 Hz), 31.7 (4-CH_3, *eq*), 43.6 d (C^5, $^3J_{\text{CP}}$ = 16.1 Hz), 59.7 d.t (**C**H_2CF_2, $^2J_{\text{CF}}$ = $^2J_{\text{CP}}$ = 26.5 Hz), 67.8 d (C^6, $^2J_{\text{CP}}$ = 6.1 Hz), 75.9 d (C^4, $^2J_{\text{CP}}$ = 6.1 Hz), 107.6 t.t (HCF_2, $^1J_{\text{CF}}$ = 254.3, $^2J_{\text{CF}}$ = 31.4 Hz), 110.4 t.t (HCF_2**C**F_2, $^1J_{\text{CF}}$ = 264.0, $^2J_{\text{CF}}$ = 30.6 Hz), 111.0 t.t (**C**$\text{F}_2\text{CF}_2\text{CH}_2$, $^1J_{\text{CF}}$ = 265.0, $^2J_{\text{CF}}$ = 30.0 Hz), 115.2 t.t.d (**C**F_2CH_2, $^1J_{\text{CF}}$ = 255.8, $^2J_{\text{CF}}$ = 31.0, $^3J_{\text{CP}}$ = 7.3 Hz); *trans* isomer (*eq*,*ax*), 22.7 d (6-CH_3, $^3J_{\text{CP}}$ = 3.2 Hz), 28.0 (4-CH_3, *ax*), 32.6 d (4-CH_3, *eq*, $^3J_{\text{CP}}$ = 4.1 Hz), 46.1 d (C^5, $^3J_{\text{CP}}$ = 5.5 Hz), 59.9 d.t (**C**H_2CF_2, $^2J_{\text{CF}}$ = 26.0, $^2J_{\text{CP}}$ = 24.9 Hz), 62.8 d (C^6, $^2J_{\text{CP}}$ = 2.9 Hz), 76.6 d (C^4, $^2J_{\text{CP}}$ = 7.4 Hz), 107.6 t.t (HCF_2, $^1J_{\text{CF}}$ = 254.3, $^2J_{\text{CF}}$ = 31.4 Hz), 110.4 t.t (HCF_2**C**F_2, $^1J_{\text{CF}}$ = 264.0, $^2J_{\text{CF}}$ = 30.6 Hz), 111.0 t.t (**C**$\text{F}_2\text{CF}_2\text{CH}_2$, $^1J_{\text{CF}}$ = 265.0, $^2J_{\text{CF}}$ = 30.0 Hz), 115.2 t.t.d (**C**F_2CH_2, $^1J_{\text{CF}}$ = 255.8, $^2J_{\text{CF}}$ = 31.0, $^3J_{\text{CP}}$ = 7.3 Hz). ^{19}F NMR spectrum, δ_F, ppm: *cis* isomer (*eq*,*eq*): –137.4 d.m (CHF_2, $^2J_{\text{FH}}$ = 52.0 Hz), –130.4 m (C**F**$_2\text{CHF}_2$), –125.3 m (C**F**$_2\text{CF}_2\text{CHF}_2$), –120.2 m ($\text{CH}_2\text{CF}_2$); *trans* isomer (*eq*,*ax*): –137.4 d.m (CHF_2, $^2J_{\text{FH}}$ = 52.0 Hz), –130.4 m (C**F**$_2\text{CHF}_2$), –125.4 m (C**F**$_2\text{CF}_2\text{CHF}_2$), –120.5 m ($\text{CH}_2\text{CF}_2$). ^{31}P NMR spectrum, δ_P, ppm: 130.5 t ($^4J_{\text{PF}}$ = 6.3 Hz, *trans*), 131.4 t ($^4J_{\text{PF}}$ = 6.3 Hz, *cis*). Found, %: C 34.76; H 4.13; F 40.04; P 8.01. $\text{C}_{11}\text{H}_{15}\text{F}_8\text{O}_3\text{P}$. Calculated, %: C 34.93; H 4.00; F 40.19; P 8.19.

General procedure for the synthesis of 1,3,2-dioxaphosphinanes 8d and 8e. A solution of 16.7 g (0.05 mol) of 2,2,3,3,4,4,5,5-octafluoropentyl phosphorodichloridite (**9**) in 150 mL of diethyl ether was cooled to –10 to –5°C, and a solution of 0.05 mol of propane-1,3-diol (**10a**) or 2,2-dimethylpropane-1,3-diol (**10b**) and 7.9 g (0.1 mol) of pyridine in 15 mL of diethyl ether was added dropwise over a period of 2 h with stirring at that temperature. Pyridine hydrochloride separated from the mixture as a white solid. The cooling bath was removed, and the mixture was stirred for 3 h at room temperature and left overnight. The precipitate was filtered off and washed with diethyl ether (3×20 mL). The filtrate was combined with the washings, the solvent was distilled off under reduced pressure, and the residue was distilled in a vacuum.

2-(2,2,3,3,4,4,5,5-Octafluoropentyloxy)-1,3,2-dioxaphosphinane (8d). Yield 7.6 g (45%), transparent liquid, bp 73–74°C (1 mm), d_4^{20} = 1.5228, n_D^{20} = 1.3804. IR spectrum, ν, cm^{-1}: 2975 s, 2940 m, 2902 s, 2846 w, 1674 w, 1638 w, 1541 w, 1480 w, 1466 w, 1431 w, 1402 w, 1373 w, 1361 w, 1331 w, 1302 w, 1290 m, 1280 m, 1264 m, 1240 s, 1172 s, 1132 s, 1095 s, 1056 s, 1016 w, 992 m, 958 m, 938 s, 902 m, 891 m, 867 s, 809 m, 770 s, 745 s, 729 s, 689 m, 675 w, 629 w, 602 m, 574 w, 562 w, 547 m, 539 m, 522 w, 505 m, 449 w, 411 m, 395 m. ^{1}H NMR spectrum, δ, ppm: 1.61 d.t.t.d (1H, 5-H_{eq}, $^2J_{\text{HH}}$ = 14.4, $^3J_{\text{H-}eq\text{,H-}ax}$ = 4.5, $^3J_{\text{H-}eq\text{,H-}eq}$ = $^4J_{\text{HP}}$ = 2.0 Hz), 2.47 d.t.t (1H, 5-H_{ax}, $^2J_{\text{HH}}$ = 14.4, $^3J_{\text{H-}ax\text{,H-}ax}$ = 12.8, $^3J_{\text{H-}ax\text{,H-}eq}$ = 4.5 Hz), 3.85 d.d.d.d (2H, 4-H_{eq}, 6-H_{eq}, $^2J_{\text{HH}}$ = 12.8, $^3J_{\text{HP}}$ = 10.0, $^3J_{\text{H-}eq\text{,H-}ax}$ = 4.5, $^3J_{\text{H-}eq\text{,H-}eq}$ = 2.0 Hz), 4.27 t.d (2H, CH_2CF_2, $^3J_{\text{HF}}$ = 13.8, $^3J_{\text{HP}}$ = 7.4 Hz), 4.48 br.t (2H, 4-H_{ax}, 6-H_{ax}, $^2J_{\text{HH}}$ = 12.8, $^3J_{\text{H-}ax\text{,H-}ax}$ = 12.8 Hz), 6.07 t.t (1H, CHF_2, $^2J_{\text{HF}}$ = 52.1, $^3J_{\text{HF}}$ = 5.6 Hz). ^{13}C NMR spectrum, δ_C, ppm: 28.2 d (C^5, $^3J_{\text{CP}}$ = 5.5 Hz), 59.9 d (C^4, C^6, $^2J_{\text{CP}}$ = 1.8 Hz), 60.1 t.d (**C**H_2CF_2, $^2J_{\text{CF}}$ = 26.7, $^2J_{\text{CP}}$ = 21.3 Hz), 107.7 t.t (HCF_2, $^1J_{\text{CF}}$ = 254.4, $^2J_{\text{CF}}$ = 31.0 Hz), 110.1 t.t (HCF_2**C**F_2, $^1J_{\text{CF}}$ = 264.6, $^2J_{\text{CF}}$ = 30.8 Hz), 111.0 t.t (HCF_2CF_2**C**F_2, $^1J_{\text{CF}}$ = 264.5, $^2J_{\text{CF}}$ = 31.6 Hz), 115.2 t.t.d (**C**F_2CH_2, $^1J_{\text{CF}}$ = 256.7, $^2J_{\text{CF}}$ = 30.4, $^3J_{\text{CP}}$ = 6.1 Hz). ^{19}F NMR spectrum, δ_F, ppm: –137.4 d.m (CHF_2, $^2J_{\text{FH}}$ = 52.1 Hz), –130.3 m (C**F**$_2\text{CHF}_2$), –125.3 m (C**F**$_2\text{CF}_2\text{CHF}_2$), –120.5 m ($\text{CH}_2$C**F**$_2$). ^{31}P NMR spectrum: δ_P 132.2 ppm. Found, %: C 28.30; H 2.50; F 45.50; P 9.39. $\text{C}_8\text{H}_9\text{F}_8\text{O}_3\text{P}$. Calculated, %: C 28.59; H 2.70; F 45.22; P 9.22.

5,5-Dimethyl-2-(2,2,3,3,4,4,5,5-octafluoropentyloxy)-1,3,2-dioxaphosphinane (8e). Yield 9.7 g (53%), transparent liquid, bp 82°C (1 mm), d_4^{20} = 1.4467, n_D^{20} = 1.3839. IR spectrum, ν, cm^{-1}: 2965 s, 2939 s, 2912 m, 2889 s, 1722 w, 1674 w, 1632 w, 1475 s, 1464 s, 1399 s, 1372 m, 1331 m, 1309 s, 1303 s, 1290 s, 1246 s, 1224 s, 1173 s, 1133 s, 1098 s, 1052 s, 1009 s, 964 s, 944 s, 910 s, 902 s, 867 w, 809 s, 793 s, 784 s, 754 s, 704 s, 689 s, 674 m, 624 s, 608 m, 573 m, 563 m, 546 m, 538 m, 522 w, 506 w, 461 m, 415 m, 383 m.

^{1}H NMR spectrum, δ, ppm: 0.75 s (3H, Me), 1.25 s (3H, Me), 3.37 t (2H, 4-H$_{eq}$, 6-H$_{eq}$, $^2J_{\mathrm{HH}}$ = 10.8, $^3J_{\mathrm{HP}}$ = 10.8 Hz), 4.13 br.d (2H, 4-H$_{ax}$, 6-H$_{ax}$, $^2J_{\mathrm{HH}}$ = 10.8 Hz), 4.24 t.d (2H, CH_2CF_2, $^3J_{\mathrm{HF}}$ = 13.9, $^3J_{\mathrm{HP}}$ = 7.3 Hz), 6.06 t.t (1H, CHF_2, $^2J_{\mathrm{HF}}$ = 52.1, $^3J_{\mathrm{HF}}$ = 5.5 Hz). ^{13}C NMR spectrum, δ_C, ppm: 22.2 (CH_3), 22.5 (CH_3), 32.6 d (C^5, $^3J_{\mathrm{CP}}$ = 4.4 Hz), 60.0 t.d ($\mathbf{C}H_2CF_2$, $^2J_{\mathrm{CF}}$ = 26.4, $^2J_{\mathrm{CP}}$ = 21.6 Hz), 69.3 (C^4, C^6), 107.7 t.t (HCF_2, $^1J_{\mathrm{CF}}$ = 254.3, $^2J_{\mathrm{CF}}$ = 31.0 Hz), 110.1 t.t ($HCF_2\mathbf{C}F_2$, $^1J_{\mathrm{CF}}$ = 265.2, $^2J_{\mathrm{CF}}$ = 31.0 Hz), 111.0 t.t ($\mathbf{C}F_2CF_2CH_2$, $^1J_{\mathrm{CF}}$ = 265.6, $^2J_{\mathrm{CF}}$ = 30.4 Hz), 115.1 t.t.d ($\mathbf{C}F_2CH_2$, $^1J_{\mathrm{CF}}$ = 256.4, $^2J_{\mathrm{CF}}$ = 30.6, $^3J_{\mathrm{CP}}$ = 6.3 Hz). ^{19}F NMR spectrum, δ_F, ppm: –137.4 d.m (CHF_2, $^2J_{\mathrm{FH}}$ = 52.1 Hz), –130.4 m ($C\mathbf{F}_2CHF_2$), –125.4 m ($C\mathbf{F}_2CF_2CHF_2$), –120.6 m (CH_2CF_2). ^{31}P NMR spectrum: δ_P 123.6 ppm, t ($^4J_{\mathrm{PF}}$ = 5.7 Hz). Found, %: C 33.21; H 3.72; F 42.02; P 8.62. $C_{10}H_{13}F_8O_3P$. Calculated, %: C 32.98; H 3.60; F 41.74; P 8.51.

ACKNOWLEDGMENTS

This study was performed under financial support by the President of the Russian Federation (program for support of leading scientific schools, project no. NSh-7145.2016.3) using the facilities of the Baikal Joint Analytical Center, Siberian Branch, Russian Academy of Sciences.

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