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Specific Features of Reaction of 2-R-Benzo[*e*][1,3,2]dioxaphosphinin-4-ones with Perfluorodiacetyl. Synthesis and Steric Structure of 4',5'-Bis(trifluoromethyl)-4-oxo-2-(2,2,3,3-tetrafluoropropoxy)-2λ^5-spiro[benzo[*e*][1,3,2]dioxaphosphinine-2,2'-[1,3,2]dioxaphosphole]

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Abstract — 2-R-benzo[*e*][1,3,2]dioxaphosphinin-4-ones react with perfluorodiacetyl under mild conditions to form relatively labile spirophosphoranes containing a 1,3,2-dioxaphosphole ring. These compounds gradually convert to more stable 2-R-4,5-bis(trifluoromethyl)-1,3,2λ^5-dioxaphosphole 2-oxides and diastereomeric 2-R-4-(trifluoroacetyl)-4-(trifluoromethyl)benzo[*f*][1,3,2λ^5]dioxaphosphepine 2-oxides, whose structure was confirmed by means of NMR and IR spectroscopy. The structure of 4',5'-bis(trifluoromethyl)-4-oxo-2-(2,2,3,3-tetrafluoropropoxy)-2λ^5-spiro[benzo[*e*][1,3,2]dioxaphosphinine-2,2'-[1,3,2]dioxaphosphole] was confirmed by X-ray diffraction analysis.

Fluorine-containing α-dicarbonyl compounds, such as perfluorodiacetyl, readily react with various P(III) derivatives to form such P(V) compounds as 4,5-bis-(trifluoromethyl)-1,3,2-dioxaphospholes (for reviews, see [1, 2]). The latter compounds are important as phosphorus-containing models of cyclic P(V) intermediates of enzymatic reactions [3–7]. Recently first representatives of stable phosphoranes in the series of bicyclophosphorylated carbohydrates were prepared by the reaction of perfluorodiacetyl with 1,2-*O*-isopropylidene-α-D-glucofuranose 3,5,6-bicyclophosphite [8]. It is known that unsymmetrical perfluorinated α-diketones, such as 4-(trifluoromethyl)perfluoropentane-2,3-dione and perfluorinated hexane-2,3-dione, react with 2-bis(2-chloroethyl)aminobenzo[*e*][1,3,2]dioxaphosphinin-4-one to form heteroring enlargement products, viz. 2-R-5-R_FCO-5-R'_F-6,7-benzo-1,3,2λ^5-dioxaphosphepin-5-one 2-oxides [9]; therewith, the reaction occurs with a relatively low selectivity, involving both carbonyl groups of the α-diketone [R_F, R'_F = CF_3, C_3F_7; C_3F_7, CF_3; CF_3, $CF(CF_3)_2$; CF_3, $CF(CF_3)_2$; $CF(CF_3)_2$, CF_3].

Continuing the cycle of works on the synthesis of functionalyzed derivatives of seven-membered heterocycles, 6,7-benzo-1,3,2- and 6,7-benzo-1,4,2-dioxaphosphepines [10–12], in the present communication we present the results of investigation of reactions of 2-R-benzo[*e*][1,3,2]dioxaphosphinin-4-ones **I** with perfluorodiacetyl (for the preliminary report, see [13]). The latter, unlike the compounds studied by Kadyrov *et al*. [9], contains equivalent carbonyl groups, which allows one to avoid formation of the mentioned regioisomers. However, it was found that the reactions with perfluorodiacetyl occur under mild conditions (–25°C, CH_2Cl_2) and give rise not to ring enlargement products, benzophosphepines, but P(V) derivatives, 1,3,2λ^5-dioxaphospholes **II** containing the starting benzophosphinine ring. The yields of these compounds reach 90–95%. The structure of the products was established by means of IR and NMR spectroscopy. The ^{31}P NMR spectra of these compounds in CH_2Cl_2 contain upfield signals in the range –54 to –57 ppm (**IIa**–**IId**) and –33.1 ppm (**IIe**), characteristic of pentaalkoxyspirophosphoranes with one five-membered ring. The IR spectra contain strong bands due to stretching vibrations of the C(O)O group

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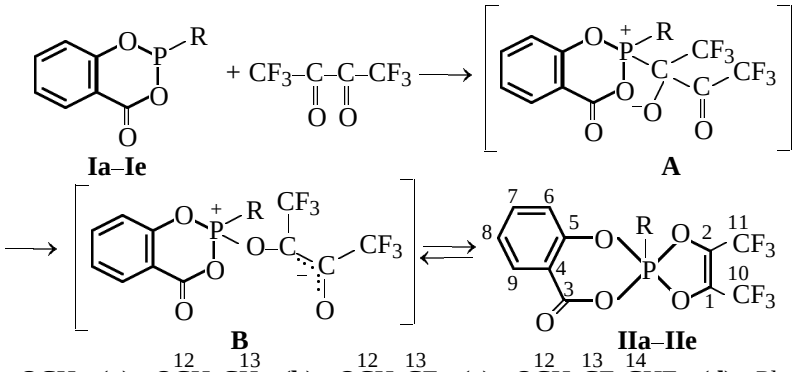
Table 1. ^{13}C–{^1H} and ^{13}C NMR spectral parameters of phosphoranes **IIb**–**IId** ($CDCl_3$–CH_2Cl_2 ~1 : 1), δ_C, ppm (*J*, Hz)

Atom	Compound **IIb**	Compound **IIc**	Compound **IId**[a]
$C^{1,2}$	129.36 br.q.m (br.q.m)[b] (45.6, $FCC^{1,2}$; 4.0–4.1, $POC^{1,2}$)	130.43 br.q.m (br.q.m) (45.3, $FCC^{1,2}$; 4.0, $POC^{1,2}$)	129.44 br.q.m (45.7, $FCC^{1,2}$; 5.2, $POC^{1,2}$)
C^3	158.87 d (d.d) (8.1, POC^3; 4.1, HC^9CC^3)	158.38 d (d.d) (8.5, POC^3; 4.0, HC^9CC^3)	157.44 d (8.5, POC^3)
C^4	114.19 d (m) (2.2, $POCC^4$; 6.9–7.1, HC^6CC^4; 6.9–7.1, HC^8CC^4)	153.69 d (m) (5.6, POC^5)	113.23 d (2.2, $POCC^4$)
C^5	153.68 d (m) (5.6, POC^5) 114.11 d (m) (2.1, $POCC^4$)	113.23 d (2.2, $POCC^4$)	152.74 d (5.7, POC^5)
C^6	119.52 d (d.d. d.d) (15.6, $POCC^6$; 166.1, HC^6; 7.7, HC^8CC^6; 1.7, HC^7C^8)	119.81 d (d.d.d) (166.1, HC^6; 15.8, $POCC^6$; 7.3, HC^8CC^6)	118.89 d (15.8, $POCC^6$)
C^7	137.50 d (d.d.d) (162.5, HC^7; 8.9, HC^9CC^7; 1.6, $POC^5C^6C^7$)	138.10 d (d.d.d) (162.2, HC^7; 7.9, HC^9CC^7; 2.0, $POC^5C^6C^7$)	137.13 s
C^8	125.70 s (d.d) (164.4, HC^8; 7.2, HC^6CC^8)	126.36 s (d.d) (164.3, HC^8; 6.8, HC^6CC^8)	125.45 s
C^9	130.94 s (br.d.d) (165.4, HC^9; 7.4, HC^7CC^9)	131.43 s (d.d) (165.4, HC^9; 6.7, HC^7CC^9)	130.59 s
$C^{10,11}$	118.95 q.d (q.d) (270.0, $FC^{10,11}$; 19.9, $POCC^{10,11}$)	118.91 q.d (q.d) (270.0, $FC^{10,11}$; 20.0, $POCC^{10,11}$)	117.88 q.d (269.0, $FC^{10,11}$; 19.9, $POCC^{10,11}$)
C^{12}	69.12 d (t.d.q) (151.1, HC^{12}; 11.7, POC^{12}; 4.5, $HC^{13}C^{12}$)	67.10 q.d (t.q.d) (154.0, HC^{12}; 37.8, $FC^{13}C^{12}$; 10.3, POC^{12})	65.65 t.d (30.5, $FC^{13}C^{12}$; 10.5, POC^{12})
C^{13}	16.15 d (q.d.t) (127.4, HC^{13}; 7.7, POCC13; 2.6, $HC^{12}C^{13}$)	22.93 q.d (q.d.t) (277.4, FC^{13}; 11.4, $POCC^{13}$; 4.4, $HC^{12}C^{13}$)	110.76 t.t.d (248.0, FC^{13}; 37.5, $FC^{12}C^{13}$; 13.0, $POCC^{13}$)

[a] C^{14}, 109.90 t.t (250.0, FC^{14}; 36.5, $FC^{13}C^{14}$). [b] Parenthesized are the signal multiplicities of the ^{13}C NMR spectra.

(1750–1770 cm^{-1}) and OC=CO multiple bond (1660–1670 cm^{-1}). It should be noted that spirophosphoranes **IIa**–**IIc** and **IIf** (viscous oils) and **IId** (crystals) are stable for some time in such solvents as CH_2Cl_2 and $CDCl_3$, which allowed their unambiguous structural assessment by means of ^1H and ^{19}F (see Experimental), as well as ^{13}C NMR spectroscopy (see Table 1). The ^{19}F NMR spectra contain a broadened singlet at –64 to –66 ppm from trifluoromethyl fluorines.

In the downfield region of the ^{13}C NMR spectra, there are C^3 and C^5 signals (157.4–158.8 and 152.7–153.7 ppm, respectively) with characteristic constants $^2J_{POC}$ 8.1–8.5 and $^2J_{POC^5}$ 5.6–5.7 Hz. The C^4 signal locates upfield (113.23–114.19 ppm, $^3J_{POCC^4}$ 2.1–2.2 Hz). The C^6–C^9 signals were assigned considering the small difference in the *ortho*- and *para*-shielding effects of the O^1 atom, deshielding effect of the COO substituent, and corresponding signal multiplicities. The dioxaphosphole C^1 and C^2 signals appear at 129.3–130.4 ppm as a characteristic quartet of doublets with the constants $^2J_{FCC^{1,2}}$ 45.3–45.7 and $^2J_{POC^{1,2}}$ 4.0–5.2 Hz. The trifluoromethyl carbon signals, too, give a quartet of doublets ($^1J_{FC^{10,11}}$ 269.0–270.0 and $^3J_{POCC^{10,12}}$ 19.9–20.0 Hz) in a fairly downfield region (117–119 ppm).



R = OCH_3 (**a**), $O\overset{12}{C}H_2\overset{13}{C}H_3$ (**b**), $O\overset{12}{C}H_2CF_3$ (**c**), $O\overset{12}{C}H_2\overset{13}{C}F_2\overset{14}{C}HF_2$ (**d**), Ph (**e**).

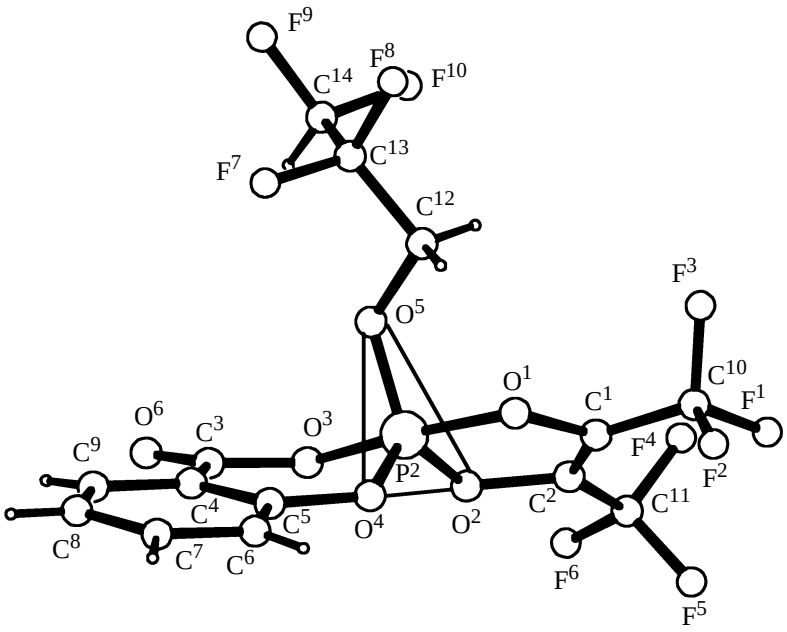


Fig. 1. Molecular geometry of spirophosphorane **IId** in crystal (the base of the trigonal bipyramid is shown by thin lines).

The reaction evidently involves initial attack of the phosphorus atom of phosphite **I** on the carbonyl carbon atom of perfluorodiacetyl with intermediate formation of dipolar ion **A** with a P^+–C–O^- fragment. Ion **A** further rearranges into dipolar ion **B** containing a P^+–OC^- bond. The main direction of further stabilization of ion **B** in which the negative charge is delocalized in the $C(CF_3)$–$C(CF_3)$–O triad is the attack of the oxygen atom on phosphorus, leading to λ^5-phosphole **II**. It is hard to tell why perfluorodiacetyl, unlike unsymmetrical perfluoro-α-diketones [9], reacts with benzophosphininones **I** in such a manner. Probably, this is connected with peculiar features of the electronic structure of this compound. Dibenzoyl behaves similarly in reactions with compounds **Ia** and **Ic** [14], but the related "salicyl" λ^5-phospholes, being unstable, could only be detected by spectral methods. By contrast, tetrachloro-*o*-benzoquinone forms a stable "salicyl" P(V) derivative in reaction with benzophosphininone **Ic** [15].

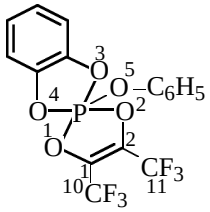
Tetrafluoropropoxy derivative **IId** well crystallizes form methylene chloride as coarse crystals, and its structure could also be confirmed by low-temperature X-ray diffraction analysis. The steric structure of compound **IId** in crystal is shown in Fig. 1, and the atomic coordinates in and selected parameters of this molecule (bond lengths and bond and torsion angles) are listed in Tables 2 and 3.

The configuration of the phosphorus atom in phosphorane **IId** is close to a regular trigonal bipyramid. The O^2, O^4, O^5, and P^2 atoms are situated in the base of the bipyramid and form an ideal plane within 0.000(1) A. The sum of the $O^4P^2O^5$, $O^2P^2O^4$, and $O^2P^2O^5$ bond angles is 360.0(1)°. The O^1 and O^3 atoms that occupy apical positions deviate from this plane by slightly different distances, 1.712(1) and –1.641(1) Å [the P^2–O^1 and P^2–O^3 bond lengths are 1.716(3) and 1.658(3) Å]. The P^2–O^2, P^2–O^4, and P^2–O^5 bonds lying in the base of the bipyramid are correspondingly shorter [1.628(2), 1.589(3), and 1.580(3) Å]. At the same time, the lengths of the exo- and endocyclic P^2–O^5 and P^2–O^4 bonds are almost the same. It is interesting to note that spirophosphorane **III** considered in [16] and structurally close to spirophosphorane **IId** has a much smaller difference between axial and equatorial bond lengths. In **III**, the axial P^2–O^1 and P^2–O^3 bonds are 1.691 and 1.693 Å, and the equatorial P^2–O^2, P^2–O^4, and P^2–O^5 bonds are 1.652, 1.636, and 1.588 Å, respectively. The configuration of molecule **III** is more distorted to a square pyramid, and the difference between the P^2–O^1 and P^2–O^3 bond lengths in the 1,3,2-dioxaphosphole ring is smaller (0.039 Å) than in **IId** [0.088(3) Å]. The asymmetry of this ring is stronger in the latter molecule. The difference in the O^2–C^2 and O^1–C^1 bond lengths is 0.024(5) Å, while in molecule **III** it is within the experimental error (0.003 Å). The axial–equatorial arrangement of the 1,3,2-dioxaphosphole ring and the difference in the lengths of in-pair equal bonds is notable even at a longer distance from O^1 and O^2. The C^2–C^{11} and

Table 2. Atomic coordinates, equivalent thermal parameters of non-hydrogen atoms $B = 4/3\sum_{i=1}^{3}\sum_{j=1}^{3}(a_i a_j)B(i, j)$ (Å^2), and isotropic thermal parameters of hydrogen atoms B_{iso} (Å^2) in molecule **IId**

Atom	*x*	*y*	*z*	*B* or B_{iso}	Atom	*x*	*y*	*z*	*B* or B_{iso}
P^2	0.49113(8)	0.13279(7)	0.37310(8)	0.0121(3)	C^3	0.3794(3)	0.1304(3)	0.5621(3)	0.0150(13)
F^1	0.8086(2)	0.1117(2)	0.1237(2)	0.0319(9)	C^4	0.2976(3)	0.2079(3)	0.5107(3)	0.0147(9)
F^2	0.6575(3)	0.21062(19)	0.0626(2)	0.0332(9)	C^5	0.3284(3)	0.2587(3)	0.4199(3)	0.0147(9)
F^3	0.6122(3)	0.0679(2)	0.0457(2)	0.0371(10)	C^6	0.2601(3)	0.3369(3)	0.3771(3)	0.0176(13)
F^4	0.8871(2)	0.00233(19)	0.3272(3)	0.0392(10)	C^7	0.1530(3)	0.3625(3)	0.4231(4)	0.0213(9)
F^5	0.9452(2)	0.1404(2)	0.3593(4)	0.0595(13)	C^8	0.1172(3)	0.3112(3)	0.5117(4)	0.0213(9)
F^6	0.8827(3)	0.0612(4)	0.4924(3)	0.099(2)	C^9	0.1887(3)	0.2347(3)	0.5564(3)	0.0197(13)
F^7	0.1268(2)	0.02083(19)	0.2516(2)	0.0299(9)	C^{10}	0.6823(3)	0.1304(3)	0.1166(3)	0.0163(9)
F^8	0.1617(2)	–0.04915(19)	0.0960(2)	0.0294(8)	C^{11}	0.8604(3)	0.0789(3)	0.3799(4)	0.0215(10)
F^9	0.1316(3)	–0.1647(2)	0.2681(3)	0.0421(10)	C^{12}	0.3367(3)	0.0306(3)	0.2090(3)	0.0162(13)
F^{10}	0.3288(3)	–0.1670(2)	0.2317(3)	0.0426(10)	C^{13}	0.2171(3)	–0.0289(3)	0.2092(3)	0.0182(13)
O^1	0.5240(2)	0.15064(19)	0.2371(2)	0.0155(5)	C^{14}	0.2436(4)	–0.1155(3)	0.2790(4)	0.0234(14)
O^2	0.6468(2)	0.11297(19)	0.4226(2)	0.0155(5)	H^6	0.28516	0.37165	0.31879	0.0214
O^3	0.4825(2)	0.11153(19)	0.5106(2)	0.0155(5)	H^7	0.10483	0.41441	0.39436	0.0256
O^4	0.4302(2)	0.23321(19)	0.3650(2)	0.0155(5)	H^8	0.04453	0.32861	0.54100	0.0256
O^5	0.3852(2)	0.05597(19)	0.3286(2)	0.0151(8)	H^9	0.16506	0.20108	0.61634	0.0235
O^6	0.3678(3)	0.0870(2)	0.6464(2)	0.0218(9)	H^{12A}	0.40260	–0.00347	0.17913	0.0194
C^1	0.6499(3)	0.1298(3)	0.2335(4)	0.0163(9)	H^{12B}	0.31259	0.08467	0.16074	0.0194
C^2	0.7207(3)	0.1084(3)	0.3378(4)	0.0215(10)	H^{14}	0.28083	–0.10188	0.36146	0.0282

C^1–C^{10} bond lengths, too, differ by 0.022(6) Å. Like in **III**, the C–F bond lengths in spirophosphorane **IId** differ from each other and are within 1.312(6)–1.339(5) Å. The respective bond lengths in molecule **III** span a slightly larger range (1.200–1.344 Å).



III

The degree of distortion of the trigonal phosphorus bipyramid in **IId** can also be judged about by the deviations of the sums of bond angles from the ideal value of 180° in three planes ($O^1O^3O^4P^2$, $O^1O^3O^2P^2$, and $O^1O^3O^5P^2$) orthogonal to the bipyramid base ($O^2O^4O^5P^2$). Hence, the sums of the OPO angles in these three planes [each of them is planar within 0.065(1), 0.006(1), and 0.070(1) Å] are 185.1(1),

Table 3. Selected bond lengths (*d*, Å) and bond (φ, deg) and torsion angles (τ, deg) in molecule **IId**

Bond	*d*	Bond	*d*	Bond	*d*
P^2–O^1	1.716(3)	F^7–C^{13}	1.361(4)	C^1–C^{10}	1.475(6)
P^2–O^2	1.628(2)	F^8–C^{13}	1.359(4)	C^2–C^{11}	1.497(5)
P^2–O^3	1.658(3)	F^9–C^{14}	1.352(5)	C^3–C^4	1.464(6)
P^2–O^4	1.589(3)	F^{10}–C^{14}	1.365(5)	C^4–C^5	1.386(5)
P^2–O^5	1.580(3)	O^1–C^1	1.356(4)	C^4–C^9	1.408(5)
F^1–C^{10}	1.329(4)	O^2–C^2	1.380(5)	C^5–C^6	1.379(6)
F^2–C^{10}	1.327(5)	O^3–C^3	1.366(4)	C^6–C^7	1.388(5)
F^3–C^{10}	1.339(5)	O^4–C^5	1.401(4)	C^7–C^8	1.390(6)
F^4–C^{11}	1.331(5)	O^5–C^{12}	1.431(4)	C^8–C^9	1.380(6)
F^5–C^{11}	1.316(5)	O^6–C^3	1.198(5)	C^{12}–C^{13}	1.518(5)
F^6–C^{11}	1.312(6)	C^1–C^2	1.322(6)	C^{13}–C^{14}	1.495(6)

Table 3. (Contd.)

Angle	φ	Angle	φ	Angle	φ
$O^1P^2O^2$	88.7(1)	$O^1C^1C^{10}$	116.1(3)	$F^2C^{10}C^1$	112.7(3)
$O^1P^2O^3$	171.6(1)	$C^2C^1C^{10}$	131.6(3)	$F^3C^{10}C^1$	111.6(3)
$O^1P^2O^4$	87.8(1)	$O^2C^2C^1$	111.3(3)	$F^4C^{11}F^5$	105.7(3)
$O^1P^2O^5$	93.7(1)	$O^2C^2C^{11}$	115.4(4)	$F^4C^{11}F^6$	106.8(4)
$O^2P^2O^3$	82.9(1)	$C^1C^2C^{11}$	133.2(4)	$F^4C^{11}C^2$	111.8(3)
$O^2P^2O^4$	122.7(1)	$O^3C^3O^6$	118.8(4)	$F^5C^{11}F^6$	109.5(4)
$O^2P^2O^5$	124.4(1)	$O^3C^3C^4$	114.7(3)	$F^5C^{11}C^2$	112.9(4)
$O^3P^2O^4$	97.3(1)	$O^6C^3C^4$	126.3(3)	$F^6C^{11}C^2$	109.8(3)
$O^3P^2O^5$	90.5(1)	$O^4C^5C^4$	122.0(3)	$O^5C^{12}C^{13}$	105.4(3)
$O^4P^2O^5$	112.9(1)	$O^4C^5C^6$	115.8(3)	$F^7C^{13}C^{12}$	109.1(3)
$P^2O^1C^1$	112.3(2)	$C^7C^8C^9$	120.5(3)	$F^7C^{13}C^{14}$	108.2(3)
$P^2O^2C^2$	114.8(2)	$C^4C^9C^8$	119.6(3)	$F^8C^{13}C^{12}$	107.6(3)
$P^2O^3C^3$	126.8(2)	$F^1C^{10}F^2$	107.5(3)	$F^8C^{13}C^{14}$	109.9(3)
$P^2O^4C^5$	123.2(2)	$F^1C^{10}F^3$	107.6(3)	$C^{12}C^{13}C^{14}$	115.2(3)
$P^2O^5C^{12}$	125.6(2)	$F^1C^{10}C^1$	111.0(3)	$F^9C^{14}C^{13}$	109.8(3)
$O^1C^1C^2$	112.3(4)	$F^2C^{10}F^3$	106.1(3)	$F^{10}C^{14}C^{13}$	107.6(3)
Angle	**τ**	**Angle**	**τ**	**Angle**	**τ**
$O^2P^2O^1C^1$	7.4(3)	$O^3P^2O^4C^5$	–36.6(3)	$P^2O^5C^{12}C^{13}$	–167.4(2)
$O^4P^2O^1C^1$	130.1(3)	$O^5P^2O^4C^5$	57.1(3)	$O^1C^1C^{10}F^1$	178.2(3)
$O^5P^2O^1C^1$	–117.0(3)	$O^1P^2O^5C^{12}$	–6.9(3)	$O^1C^1C^{10}F^3$	–61.8(5)
$O^1P^2O^2C^2$	–7.4(3)	$O^2P^2O^5C^{12}$	–97.9(3)	$O^2C^2C^{11}F^5$	–121.2(4)
$O^3P^2O^2C^2$	171.9(3)	$O^3P^2O^5C^{12}$	–179.6(3)	$O^2C^2C^{11}F^6$	1.3(6)
$O^4P^2O^2C^2$	–93.9(3)	$O^4P^2O^5C^{12}$	82.2(3)	$O^3C^3C^4C^9$	–179.6(3)
$O^5P^2O^2C^2$	86.2(3)	$P^2O^1C^1C^2$	–5.6(5)	$O^6C^3C^4C^9$	–3.7(6)
$O^2P^2O^3C^3$	165.7(3)	$P^2O^2C^2C^1$	5.8(5)	$O^6C^3C^4C^5$	173.5(4)
$O^4P^2O^3C^3$	43.5(3)	$P^2O^3C^3C^4$	–27.4(5)	$O^5C^{12}C^{13}C^{14}$	–61.6(4)
$O^5P^2O^3C^3$	–69.7(3)	$P^2O^3C^3O^6$	156.4(3)	$O^5C^{12}C^{13}F^8$	175.6(3)
$O^1P^2O^4C^5$	150.1(3)	$P^2O^4C^5C^6$	–160.9(3)	$F^7C^{13}C^{14}F^{10}$	176.8(3)
$O^2P^2O^4C^5$	–122.9(2)	$P^2O^4C^5C^4$	18.4(5)	$C^{12}C^{13}C^{14}F^9$	–177.0(3)

171.6(1), and 184.3(1)°. This result means that the P^2, O^1, and O^3 atoms fall roughly on the same axis.

The conformation of the five-membered ring is a strongly flattened *envelope* (Fig. 2). The phosphorus atom deviates from the $O^1C^1C^2O^2$ plane [planar within 0.001(2) Å] only slightly [0.1516(5) Å]. The entire pentaatomic $P^2O^1C^1C^2O^2$ fragment is planar within 0.046(2) Å. The O^4 and O^5 atoms deviate from this plane to opposite sides by –1.243(1) and 1.397(1) Å, while the deviation of O^3 is insignificant [0.136(1) Å]. Endocyclic bond angles at O^1, O^2, C^1, and C^2 [112.3–114.8(2)°] are significantly smaller than respective endocyclic angles in the six-membered heteroring in **IId**, as well as the exocyclic $P^2O^5C^{12}$ angle. By contrast, the exocyclic $C^2C^1C^{10}$ and $C^1C^2C^{11}$ angles in structures **IId** and **III** are larger by about 20°. This is evidently connected with the steric repulsion of the electron-acceptor trifluoromethyl groups.

The second heteroring in molecule **IId** has a distorted *sofa* conformation (Fig. 3). The pentaatomic $O^3C^3C^4C^5O^4$ fragment is planar within 0.037(2) Å. The O^6 atom deviates from the plane of this fragment by only –0.0567(1) Å (the $O^6C^3C^4C^5$ and $O^3C^3C^4C^5$ dihedral angles are 173.5(4) and –2.3(5)°], and the deviation of the phosphorus atom is more significant [0.5822(5) Å].

In the related cyclic P(III) derivative **IV**, the phosphinine heteroring has a *sofa* conformation with an analogous planar fragment and a slightly greater deviation of the phosphorus atom [0.5904(6) Å]. The magnitudes of the $O^6C^3C^4C^5$ and $O^3C^3C^4C^5$ dihedral angles [178.3(3)° and 0.2(4)°, respectively]

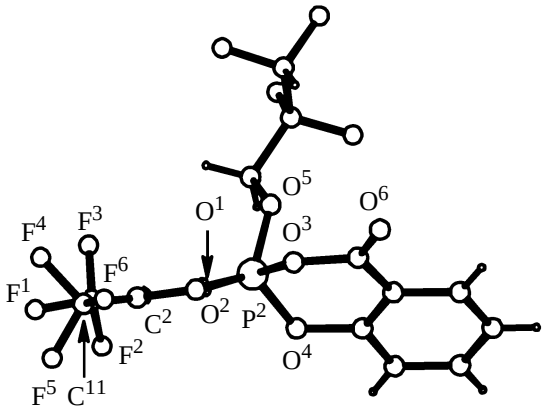


Fig. 2. *Envelope* conformation of the 1,3,2-dioxaphosphole ring in phosphorane **IId** (side view).

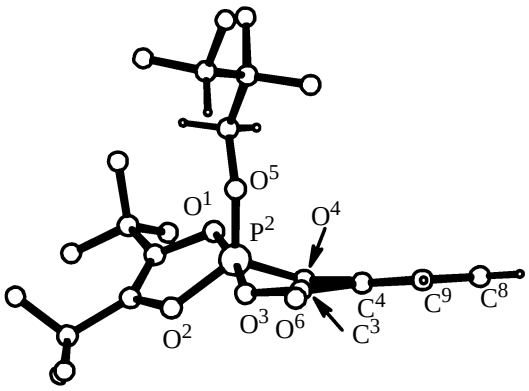
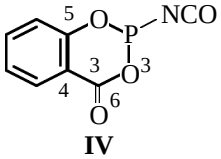


Fig. 3. *Sofa* conformation of the 1,3,4-dioxaphosphinin-4-one heteroring in phosphorane **IId** (side view).

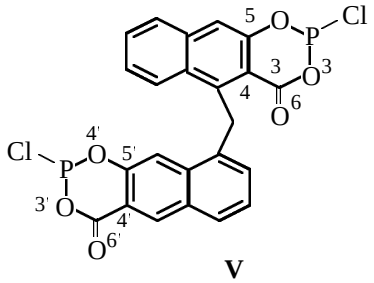
suggest a stronger planarity of the $O^3C^3C^4C^5O^4$ fragment [17] in molecule **IV**.



IV

Such flattening in both molecules is evidently connected with the favorableness of conjugation of the carbonyl group with the π system of the benzene ring. The O^1, O^2, and O^5 atoms deviate from the above plane by 1.085(1), –0,300(1), and 2.060(1) Å. Contrary to what is observed in structure **IV**, the C^3 and O^4 atoms in structure **IId** deviate from the benzene ring plane to opposite sides by –0.110 Å and 0.095(1) Å, which is probably connected with the strong tension that appears in the phosphinine heteroring with a trigonal bipyramidal phosphorus atom. The change in the coordination of the phosphorus atom produces certain changes in bond lengths and angles in this heteroring. Hence, the difference in the P^2–O^4 and P^2–O^3 bond lengths increases [0.069(3) and 0.020(2) Å in structures **IId** and **IV**, respectively]. The same relates to the O^4–C^5 and O^3–C^3 bond lengths [0.035(4) and 0.008(4) Å in structures **IId** and **IV**, respectively]. As to bond angles, then some of them ($O^3P^2O^4$ and $P2O^4C^5$) in spirophosphorane **IId** are also increased compared to those in **IV**, where they are equal to 99.4(1), 121.4(2), and 124.1(2)°, respectively.

Unlike structures **IId** and **IV**, both phosphinine heterorings in diphosphorylated bicyclic pamoic acid derivative **V** [18] have a distorted *boat* conformation, which follows from by the deviations of the P^2 ($P^{2'}$) and O^3 ($O^{3'}$) from the $C^3C^4C^5O^4$ ($C^{3'}C^{4'}C^{5'}O^{4'}$) fragment planar within 0.011 (0.019) Å to the same side by 0.62 (0.69) and 0.23 (0.28) Å, respectively. This molecule contains two more fragments [$P^2O^3 \cdot C^3(O^6)C^4$ and $P^{2'}O^{3'}C^{3'}(O^{6'})C^{4'}$] planar within 0.02 and 0.009 Å (the corresponding dihedral angles are 2.0 and 4.0°, respectively). The $O^4(O^{4'})$ and $C^5(^{5'})$ deviate to the same side from them by –0.57 (–0.65) and –0.32 (–0.38) Å, respectively. The *boat* conformation of the molecule makes the carbonyl group to deviate from the $C^3C^4C^5O^4$ ($C^{3'}C^{4'}C^{5'}O^{4'}$) plane at larger distances of –0.17 (–0.24) Å (the $O^6C^3C^4C^5$ and $O^{6'}C^{3'}C^{4'}O^{5'}$ dihedral angles are –164.9 and –169.1°).



V

The tetrafluoropropoxy group in phosphorane **IId** is equatorial. The C^{12} atom of this group is *trans* to the axial P^2–O^3 bond [the $O^3P^2O^5C^{12}$ dihedral angle is –179.6(3)°]. The P^2–O^3 and O^5–C^{12} bonds are almost eclipsed [the $O^1P^2O^5C^{12}$ dihedral angle is –6.9(3)°]. The pentaatomic $O^1O^3P^3O^5C^{12}$ fragment is planar within 0.071(2) Å. A conformation having P^2 *trans* to C^{13} atoms is realized along the O^5–C^{12} axis [the $P^2O^5C^{12}C^{13}$ dihedral angle is 167.4(2)°]. It is interesting to note that the more extended hexaatomic $O^1O^3P^2O^5C^{12}C^{13}$ fragment, too, is planar within 0.089(2) Å (*W* conformation of the $O^3P^2O^5 \cdot C^{12}C^{13}$ fragment). Such location of the acyclic tetra-

fluoropropoxy group is evidently associated with its tendency for minimum steric interactions with the other substituents in the phosphorus bipyramid. Almost ideal staggered conformations are realized along the C^{12}–C^{13} and C^{13}–C^{14} bonds. As molecule **IId** contains no labile hydrogen atoms, its crystal lacks classical hydrogen bonds. The only interactions found in its packing are of the C–H···O type: C^{14}–H^{14}···$O^{2'}$ (1 – *x*, –*y*, 1 – *z*) and C^6–H^6···$O^{6''}$ (*x*, 1/2 – *y*, –1/2 + *z*). The characteristics of these interactions are the following: C^{14}–H^{14} 0.98 Å, H^{14}···$O^{2'}$ 2.48 Å, C^{14} 3.433(5) Å, $C^{14}H^{14}O^{2'}$ 163.5°; C^5–H^6 0.93 Å, H^6···$O^{6''}$ 2.43 Å, C^6···$O^{6''}$ 3.3323(5) Å, and $C^6H^6O^{6''}$ 161.3°. The first interaction forms centrosymmetric dimers and the second binds these dimers into zigzag tapes running along the 0*z* axis (Fig. 4).

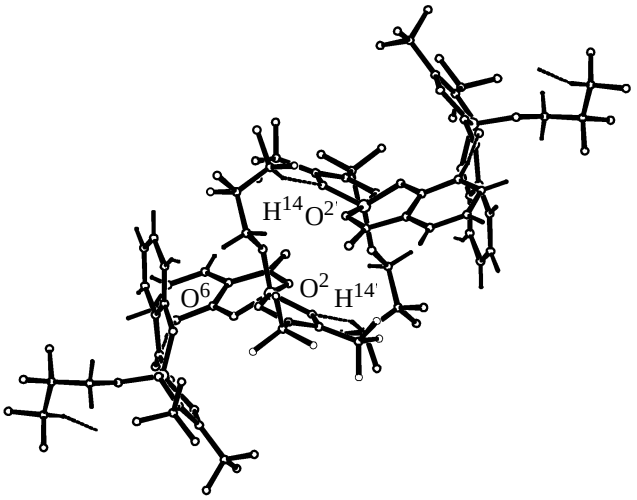
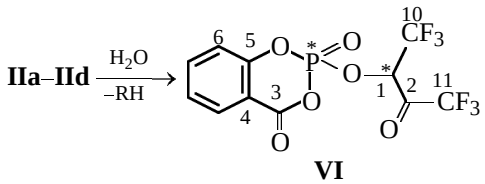


Fig. 4. System of nonclassical interactions in the crystal of compound **IId**.

Spirophosphoranes **II** are hydrolytically rather unstable and fairly rapidly decompose under the action of air moisture. Note that the 1,3,2-dioxaphosphole ring is hydrolyzed first to form diastereomeric phosphates **VI** in a 1 : 1 ratio, which can be further equally readily hydrolyzed with cleavage of the phosphinine ring. For this reason, we failed to isolate phosphates **VI** pure, but could fairly easily identify them by spectral methods.

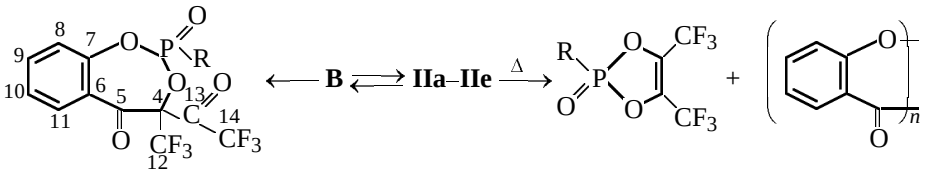


VI

In the ^{1}H NMR spectrum (400 MHz, $CDCl_3$), the proton at C^1 appears as two doublets of quartets (δ 6.38, $^3J_{POCH}$ 14.4 Hz, $^3J_{FCCH}$ 7.2 Hz; δ 5.99 ppm, $^3J_{POCH}$ 12.1 Hz, $^3J_{FCCH}$ 7.4 Hz). In the ^{13}C–{^{1}H} NMR spectrum, the C^3–C^6 signals are split into doublets due to coupling with phosphorus, which points to a cyclic structure of the phosphates. The ^{13}C NMR spectrum, too, exhibits additional multiplicity due to coupling with protons (δ_C, ppm, *J*, Hz): 153.34 br.d.d and 154.28 br.d.d (C^3, $^2J_{CCCH}$ 7.2–7.3), 111.87 m and 111.90 m (C^6, $^3J_{POCC}$ 12.4. The acyclic fluorinated substituent is also easily identified in the spectrum (δ_C, ppm; *J*, Hz): 75.16 d.q.d and 75.05 d.q.d (C^1, $^1J_{HC}$ 155.4, $^2J_{PCC}$ 35.4, $^2J_{POC}$ 4.8), 117.66 q.d and 118.10 q.d (C^{10}, $^1J_{FC}$ 270.0, $^2J_{POC}$ 19.8 and 20.7), 179.45 q.d.d and 179.20 q.d.d (C^2, $^2J_{FCC}$ 38.8 and 39.0, $^3J_{POCC}$ 5.6, $^2J_{HCC}$ 4.7 and 5.2), 120.01 q and 119.98 q (C^{11}, $^1J_{FC}$ 282.9–283.0).

On prolonged handling or on heating spirophosphoranes gradually undergo some transformations. Therewith, the upfield signals belonging to phosphoranes decrease in intensity, and signals characteristic of four-coordinate phosphorus derivatives appear (δ_P 9–12 and δ_P –10 to 14 ppm). Hence heating of phosphorane **IIa** in chloroform for 6 h gives three compounds. In ^{31}P NMR spectrum (121.42 MHz, $CHCl_3$) they are characterized by signals at δ_{P^1} 10.3 q ($^3J_{POCH}$ 12.2), δ_{P^2} –11.2 q ($^3J_{POCH}$ 11.0, and δ_{P^3} –13.3 ppm, q, ($^3J_{POCH}$ 11.0 Hz) in a 5 : 12 : 12 ratio. Heating of spirophosphorane **IIb** under analogous conditions, too, leads to formation of three compounds with δ_{P^1} 9.1 t ($^3J_{POCH}$ 9.2), δ_{P^2} –10.5 t ($^3J_{POCH}$ 9.2 Hz), and δ_{P^3} –12.2 ppm, t ($^3J_{POCH}$ 10.3 Hz) in a 1 : 2 : 2 ratio (conversion 72%). Heating of phosphorane **IIb** in toluene for 2 h results in its complete transformation to a mixture of compounds with δ_{P^1} and $\delta_{P^{2,3}}$ in a 7 : 20 ratio. For spirophosphorane **IIc** to completely transform into analogous compounds with δ_{P^1} 9.3 t ($^3J_{POCH}$ 12.1) and δ_{P^2} –12.9 ppm, t ($^3J_{POCH}$ 10.3 Hz) (7 : 10 ratio) more prolonged heating in toluene (6–8 h) is needed. Note that heating of the same phosphoranes (6–8 h) in the more polar acetonitrile increases the fraction of the reaction products with chemical shifts $\delta_{P^{2,3}}$ to 70–90% in the reaction mixture. By vacuum distillation we could only isolate compounds with δ_{P^1}, viz. decomposition products of phosphoranes **IIa**–**IIc**. On the basis of the ^{31}P, ^{19}F, and ^{1}H NMR spectra and elemental analyses, these products were assigned the structure of phospholenes **VIIa**–**VIIc**.

Hence, like spirophosphoranes containing a benzo[*e*][1,3,2]dioxaphosphinin-4-one fragment, we studied previously [10, 14, 15, 19], compounds **II** can split off oligomer **VIII** on thermolysis and form 1,3,2-

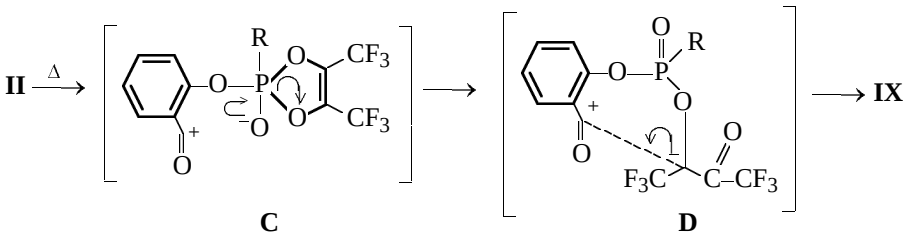


IXa–IXe **VIIa–VIIe** **VIII**

R = OCH_3 (**a**), OCH_2CH_3 (**b**), OCH_2CF_3 (**c**), $OCH_2CF_2CHF_2$ (**d**), Ph (**e**).

dioxaphospholes **VII**. Compounds with $\delta_{P^{2,3}}$ were not isolated pure because of their tendency for hydrolysis and lability under heating in the course of vacuum distillation. Nevertheless, these compounds could sufficiently reliably identified by means of ^{1}H, ^{13}C, ^{19}F, and ^{31}P NMR and IR spectra, using the corresponding enriched fractions obtained by vacuum distillation. Such analysis shows (see Experimental and Table 1) that these compounds are 1,3,2-dioxaphosphepines **IX**. Their chemical shifts ($\delta_{P^{2,3}}$) coincide with those of benzophosphepines previously obtained from methyl trifluoropyruvate [19] and hexafluoroacetone [20]. The CF_3 and $C(O)CF_3$ fluorine chemical shifts fall in the range 61–67 ppm. The IR spectra contain two types of absorption bands at 1700–1720 and 1660–1680 cm^{-1}, characteristic of trifluoromethyl-substituted and usual keto groups. The ^{13}C NMR spectrum of diastereomeric phosphepines **IXb** (see Experimental) significantly enriched with one diastereomer (8 : 1) contains signals of key carbon atoms of the phosphepine ring with expected multiplicities. Hence, in the downfield region of the spectrum, a singlet at 185.26 ppm and a quartet of doublets at 181.13 ppm, belonging respectively to the C^5 and C^{13} atoms of the endo- and exocyclic carbonyl groups, are present. In the upfield region of the spectrum, a signal of the quaternary C^4 atom with the corresponding multiplicity (broadened quartet of doublets) is observed. The signals of the rest carbon atoms were assigned on the basis of data in [19, 20].

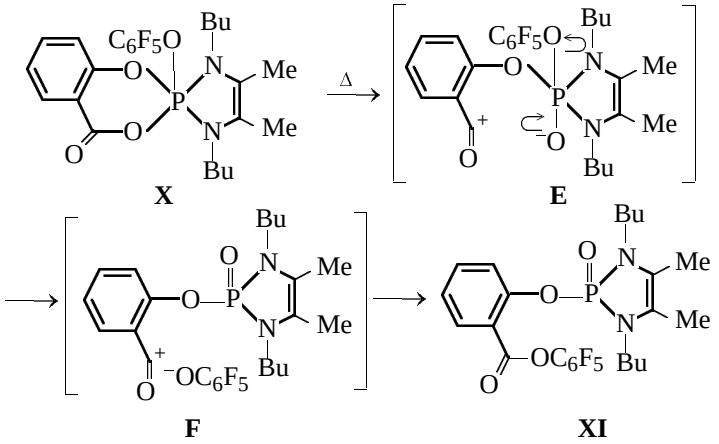
Thus, heating of spirophosphoranes **II** gives, along with 1,3,2-dioxaphospholes **VII**, 1,3,2-dioxaphosphepines **IX**. As mentioned in [21], 4,5-bis(trifluoromethyl)-1,3,2λ^5-dioxaphospholes prepared from simple phosphites can decompose to phosphates in the presence of pyridine. The unusual behavior of phosphoranes containing a benzo[*e*][1,3,2]dioxaphosphinin-4-one fragment is observed for the first time and can be considered as evidence to show either that the stage of formation of spirophosphoranes **II** from dipolar ion **B** is reversible or that both decomposition pathways of phosphorane **II** begin with cleavage of the endocyclic C(O)–OP bond and involve formation of the same intermediate. Such intermediate may, for example, have structure **C** that comprises an acylium cation and a phosphorane fragment having the alkoxide ion as one of ligands. Such acylium cations can be formed by hydrolysis of esters or under the action of strong Lewis acids on carboxylic acid anhydrides or chlorides [22]. In this case, the phosphorane fragment of the molecule acts as a leaving group which then very easily transforms into the phosphate substituent. The negative charge during this process passes to the more electron-acceptor dioxaphosphole ring, thus inducing its opening (structure **D**). Intramolecular attack of the carbanionic part of intermediate **D** on the acylium ion leads to final phosphepine **IX**.



C **D**

This proposed scheme of the transformation of phosphorane **II** to phosphepine **IX** may evidently also explain the transformation of phosphorane **X** to diazaphosphole **XI** [23].

In the latter case, too, an acylium cation containing an alkoxide–phosphorane fragment (structure **E**) is initially formed. Further on, a phosphoryl group is formed, with the pentafluorophenoxide anion playing



X **E** **F** **XI**

the role of a group leaving the phosphorus atom (structure **E**).

Hence, in this work we showed for the first time that cyclic salicyl derivatives of phosphorous acid react with perfluorodiacetyl by the way of formation of spiriphosphorane structures containing a 1,3,2-dioxaphosphole fragment. At elevated temperatures, the products undergo further thansformations mainly in two directions, viz. via formation of λ^4-1,3,2-dioxaphospholes and a salicylic acid oligomer and via formation of benzo[*f*][1,3,2]dioxaphosphepines.

EXPERIMENTAL

The NMR spectra were recorded on Bruker MSL-400 (^{13}C, 100.6 MHz; ^{31}P 162.0 MHz), Bruker WM-250 (^{13}C 62.5 MHz, ^{1}H, 250 MHz, ^{31}P, 101.6 MHz), and Varian Unity-300 (^{1}H, 300 MHz; ^{19}F 282.2 MHz) spectrometers. The spectra were measured against internal HMDS and external 85% phosphoric acid. The ^{19}F NMR spectra were obtained for solutions containing 10% of C_6F_6, and then δ_F were recalculated against $CFCl_3$. The IR spectra were recorded on a Specord M-80 spectrometer for films or suspensions in mineral oil between KBr plates. Compounds **I** were obtained as described in [20, 24, 25].

X-ray diffraction analysis of compound **IId** was carried out on an Enraf–Nonius CAD-4 automatic four-curcle diffractometer. Crystals of compound **IId** are monoclinic; at 20°C, *a* 10.420, *b* 14.560(5), *c* 11.690(5) Å, β 102.22(2)°, *V* 1733(1) Å^3, *Z* 4, d_{calc} 1.89 g cm^{-3}, space group $P2_1/c$. The cell parameters and the intensities of 2732 reflections, among which 2500 were with $I > 2\sigma(I)$, were measured at –150°C, $\lambda Cu K_\alpha$ radiation, graphite monochromator, $\omega/2\theta$ scanning, $\theta < 74.45°$. No intensity decay of three control reflections was observed during measurements. The structures were solved by the direct method using the SIR program [26] and refined by the SHELXL-97 program [27] first isotropically and then anisotropically. Hydrogen atoms were revealed by difference synthesis and included in structure amplitudes with fixed thermal and positional parameters. The final divergence factors were R 0.068 and R_W 0.185 on 2500 reflections with $F^2 > 2\sigma$. The drawings of the molecule and crystal packing, as well as calculation of intra- and intermolecular interactions were performed using the PLATON program [28].

Reaction of 2-methoxybenzo[*e*][1,3,2]dioxaphosphinin-4-one (Ia) with perfluorodiacetyl. To a mixture of 3.96 g of methyl phosphite **Ia** and 10 ml of CH_2Cl_2, a solution of 3.95 g of perfluorodiacetyl in 4 ml of CH_2Cl_2 was slowly added dropwise with stirring at –25°C. The reaction mixture was let to warm up to 20°C over the course of 30 min, and the solvent was removed in a vacuum (12 mm Hg) at a temperature of no higher than 15–20°C to obtain 4',5'-bis(trifluoromethyl)-2-methoxy-4-oxo-2λ^5-spiro-[benzo[*e*][1,3,2]dioxaphosphinine-2,2'-[1,3,2]dioxaphosphole] (**IIa**), viscous colorless oil, yield 94%. IR spectrum, ν, cm^{-1}: 2990, 2930, 2885 (CH), 1784 (C=O), 1741, 1712, 1682, 1614, 1594, 1481, 1465, 1454, 1442, 1375, 1310, 1225–1240, 1175–1180, 1122, 1060, 1020, 970, 875. ^{19}F NMR spectrum (CH_2Cl_2): δ_F –65.05 ppm (br.s). ^{31}P NMR spectrum (121.42 MHz, CH_2Cl_2, δ, ppm, *J*, Hz): δ_P –54.6 q ($^3J_{POCH}$ 16.1). Found, %: C 36.53; H 2.09. $C_{12}H_7F_6 \cdot O_6P$. Calculated, %: C 36.73; H 1.78. Compound **IIa** was further heated for 1 h at 65–68°C in $CHCl_3$ to form 2-methoxy-4,5-bis(trifluoromethyl)-1,3,2λ^5-dioxaphosphole 2-oxide (**VIIa**) and diastereomeric 2-methoxy-4-(trifluoroacetyl)-4-(trifluoromethyl)-4,5-dihydrobenzo[*f*][1,3,2λ^5]dioxaphosphepin-5-one-2-oxides **IXa** in the ratio 0.5 **IIa**:1.71 **VIIa**:1.0 (**IXa**). Upon heating for 6 h at 65-68°C in $CHCl_3$, the signal of the starting phosphorane disappeared, and a 5:24 mixture of compounds **VIIa** and **IXa** formed. The

diastereomeric ratio in phosphepine **IXa** was 1 : 1. Methoxyphosphole **VIIa** was isolated by vacuum distillation, yield 16%, bp 80°C (0.2 mm). ^{31}P NMR spectrum (121.43 MHz, CH_2Cl_2), δ_P, ppm (*J*, Hz): 13.0 q ($^3J_{POCH}$ 12.2). Found, %: C 22.17; H 1.22. $C_5H_3F_6O_4P$. Calculated, %: C 22.06; H 1.10.

Reaction of 2-ethoxybenzo[*e*][1,3,2]dioxaphosphinin-4-one (Ib) with perfluorodiacetyl was carried out by an analogous procedure. 4',5'-Bis(trifluoromethyl)-2-ethoxy-4-oxo-2λ^5-spiro[benzo[*e*][1,3,2]dioxaphosphinine-2,2'-[1,3,2]dioxaphosphole] (**IIb**) was obtained as a colorless viscous oil, yield 95%. IR spectrum, cm^{-1}: 1780, 1750, 1716, 1695, 1680, 1644, 1610, 1590 (C=O, OC=C, C=C_{arom}); 1470, 1450, 1390, 1350 (δ_{CH}); 1310, 1305, 1290 (CF, O–C); 1230, 1140–1150, 1095–1100, 1020–1030, 1000, 982, 960, 850– 860, 768. ^{1}H NMR spectrum (300 MHz, $CDCl_3$, δ, ppm, *J*, Hz): 8.03 d.d.d (H^{9*}, $^3J_{H^8CCH^9}$ 7.8, $^4J_{H^7CCCH^9}$ 0.5), 7.66 d.d.d.d (H^7, $^3J_{H^6CCH^7}$ 8.3, $^3J_{H^8CCH^7}$ 7.4, $^5J_{POCCCH^7}$ 2.0, $^4J_{H^9CCCH^7}$ 1.8), 7.30 d.d.d.d (H^8, $^3J_{H^9CCH^8}$ 7.4, $^4J_{H^6CCCH^8}$ 1.1, $^6J_{POCCCCH^8}$ 0.1), 7.20 d.d.d.d (H^6, $^3J_{H^7CCH^6}$ 8.3, $^4J_{H^8CCCH^6}$ 1.1, $^4J_{POCCH^6}$ 1.1, $^5J_{H^9CCCCH^6}$ 0.5), 4.18 m and 4.25 m ($POCH_2$, *AB* part of the *ABMX*$_3$ spectrum, $^3J_{AX} = {}^3J_{BX}$ 7.0, $^3J_{AM} = {}^3J_{BM}$ 12.3, $^3J_{AB}$ 5.5), 1.25 d.t (CH_3, $^3J_{AX} = {}^3J_{BX}$ 7.0, ^4J(POCC$_X$) 2.1). ^{19}F NMR spectrum (CH_2Cl_2), δ_F, ppm: –64.77 br.s. ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: –64.98 br.s. ^{31}P–{^{1}H} NMR spectrum (162.0 MHz, CH_2Cl_2), δ_P, ppm (*J*, Hz): –55.6 t ($^3J_{POCH}$ 12.2). Found, %: C 38.71; H 2.49. $C_{13}H_9F_6O_6P$. Calculated, %: C 38.42; H 2.22. Phosphorane **IIb** was heated in toluene for 2 h at 110°C, after which the solvent was distilled off in a vacuum to leave a viscous slightly yellowish oil comprising a 7 : 20 mixture of 4,5-bis(trifluoromethyl)-2-ethoxy-1,3,2λ^5-dioxaphosphole 2-oxide (**VIIb**) and diastereomeric 2-ethoxy-4-(trifluoroacetyl)-4-(trifluoromethyl)-4,5-dihydrobenzo[*f*][1,3,2λ^5]dioxaphosphepin-5-one 2-oxides **IXb**. ^{1}H NMR spectrum (300 MHz, $CDCl_3$ + 20% of CH_2Cl_2) of isomeric phosphepines (d_1, d_2), δ, ppm (*J*, Hz): 8.08 d.d.d (H^{11}, $^3J_{H^{10}CCH^{11}}$ 7.9, $^4J_{H^9CCCH^{11}}$ 1.8, $^5J_{H^9CCCCH^{11}}$ 0.4) (d_1), 7.84 br.d.d (H^{11}, $^3J_{H^{10}CCH^{11}}$ 7.8, $^4J_{H^9CCCH^{11}}$ 1.8) (d_2); 7.73 d.d.d.d (H^9, $^3J_{H^8CCH^9}$ 8.4, $^3J_{H^{10}CCH^9}$ 7.4, $^4J_{H^{11}CCCH^9}$ 1.8, $^5J_{POCCCH^9}$ 1.2) (d_1), 7.66 d.d.d.d (H^9, $^3J_{H^8CCH^9}$ 8.4, $^3J_{H^{10}CCH^9}$ 7.6, $^4J_{H^{11}CCCH^9}$ 1.8, $^5J_{POCCCH^9}$ 1.2) (d_2); 7.37 d.d.d.d (H^{10}, $^3J_{H^{11}CCH^{10}}$ 7.9, $^3J_{H^{11}CCH^{10}}$ 7.8, $^3J_{H^9CCH^{10}}$ 7.6, $^4J_{H^8CCCH^{10}}$ 1.1) (d_2); $^3J_{H^9CCH^{10}}$ 7.4, $^4J_{H^8CCCH^{10}}$ 1.0) (d_1), 7.35 d.d.d (H^{10}, 7.23 d.d.d.d (H^8, $^3J_{H^9CCH^8}$ 8.4, $^4J_{H^{10}CCCH^8}$ 1.0, $^4J_{POCCH^8}$ 0.9, $^5J_{H^{11}CCCCH^8}$ 0.4) (d_1), 7.26 d.d.d.d (H^8, $^3J_{H^9CCH^8}$ 8.4, $^4J_{H^{10}CCCH^8}$ 1.1, $^4J_{POCCH^8}$ 1.1, $^5J_{H^{11}CCCCH^8}$ 0.5) (d_2); 4.37–4.39 m (CH_2, $^3J_{HCCH}$ 7.1, $^3J_{POCH}$ 10.6) (d_1, d_2); 1.47 t.d (CH_3, $^3J_{HCCH}$ 7.1, $^4J_{POCCH}$ 1.1) (d_1), 1.44 t.d (CH_3, $^3J_{HCCH}$ 7.1, $^4J_{POCCH}$ 1.4) (d_2). Phosphole **VIIb** was isolated by vacuum distillation, yield 35%, bp 90°C (0.2 mm Hg). ^{31}P NMR spectrum (121.43 MHz, CH_2Cl_2), δ_P, ppm: 9.1 t ($^3J_{POCC}$ 9.2 Hz). ^{19}F NMR spectrum (CH_2Cl_2), δ_F, ppm: –65.22 br.s. ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: –65.43 br.s. Found, %: C 24.93; H 2.11. $C_6H_5 \cdot F_6O_4P$. Calculated, %: C 25.17, H 1,75. One of the fractions, enriched (88%) with one of the diastereomers of dioxaphosphepine **IXb** was also isolated by vacuum distillation, yield 27%, bp 120–123°C (0.1 mm Hg). IR spectrum, ν, cm^{-1}: 1721, 1712, 1680 (C=O), 1620, 1590, 1495, 1410 (C=C_{ar}, CH), 1360, 1320, 1310 (POC, CF, δ_{CH}), 1295 (P=O). ^{13}C–{^{1}H} NMR spectrum (the multiplicities of signals in the ^{13}C NMR spectrum are given in parentheses), δ, ppm (*J*, Hz): 87.93 br.q.d (br.q,d) (C^4, $^2J_{FCC}$ 29.0–32.0), 185.26 br.s (br.s) (C^5); 125.55 br.s (br.m) (C^6); 148.48 d (m) (C^7, $^2J_{POC}$ 9.0); 121.52 d (d.d) (C^8, $^1J_{HC}$ 167.6, $^3J_{POC}$ 7.8, $^3J_{HCCC}$ 7.8–8.0); 138.50 s (d.d) (C^9, $^1J_{HC}$ 163.6, $^3J_{HCCC}$ 9.0); 126.30 s (d.d) (C^{10}, $^1J_{CH}$ 166.4, $^3J_{HCCC}$ 7.8); 131.89 d (d.d.d.d) (C^{11}, $^1J_{HC}$ 168.0, $^3J_{HCCC}$ 8.6, $^4J_{POCCC}$ 2.4, $^2J_{HCC}$ 1.7); 118.10 q.d (q.d) (C^{12}, $^1J_{PC}$ 270.4, $^3J_{POCC}$ 20.7); 181.13 q.d (q.d) (C^{13}, $^2J_{FCC}$ 29.0–32.0, $^3J_{POCC}$ 5.9–6.4); 120.30 q (q) (C^{14}, $^1J_{PC}$ 282.9), 69.18 d (t.d.q) (CH_2, $^1J_{POC}$ 6.9, $^2J_{HCC}$ 4.2); 15.47 d (q.d.t) (CH_3, $^1J_{CH}$ 127.8, $^2J_{HCC}$ 2.5). ^{19}F NMR spectrum (CH_2Cl_2), δ_F, ppm: –61.37 br.s ($COCF_3$), –67.11 br.s (CF_3). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: –61.68 br.s ($COCF_3$), –67.26 br.s (CF_3). ^{13}P NMR spectrum (162.0 MHz, CH_2Cl_3), δ_P, ppm: –11.9 br.t ($^3J_{POCH}$ 10.6 Hz).

Reaction of 2-(2,2,2-trifluoroethoxy)benzo[*e*]-[1,3,2]dioxaphosphinin-4-one (Ic) with perfluorodiacetyl was carried out by an analogous procedure, using 10.65 g of compound **Ic**, 25 ml of CH_2Cl_2, and 7.76 g of perfluorodiacetyl in 10 ml of CH_2Cl_2. The solvent was distilled off in a vacuum (12 mm Hg) at a temperature of no higher than 15–20°C to obtain 4',5'-Bis(trifluoromethyl)-4-oxo-2-(2,2,2-trifluoroethoxy)-2λ^5-spiro[benzo[*e*][1,3,2]dioxaphosphinine-2,2'-[1,3,2]dioxaphosphole] (**IIc**) as a colorless viscous oil, yield 96%. ^{1}H NMR spectrum (300 MHz, $CDCl_3$ + 10% of CH_2Cl_2), δ, ppm (*J*, Hz): 8.04 d.d.d (H^9, 1H, $^3J_{H^8CCH^9}$ 7.9, $^4J_{H^7CCCH^9}$ 1.8, $^5J_{H^6CCCCH^9}$ 0.4); 7.69 d.d.d.d (H^7, 1H, $^3J_{H^6CCH^7}$ 8.4, $^3J_{H^8CCH^7}$ 7.4,

* Here and hereinafter, the atom numbering is that used in the corresponding structures in the text.

$^5J_{POCCCH^7}$ 1.8); 7.33 d.d.d (H^8, 1H, $^3J_{H^9CCH^8}$ 7.9, $^3J_{H^7CCH^8}$ 7.4, $^4J_{H^6CCCH^8}$ 0.9); 7.22 d.d.d.d (H^6, 1H, $^3J_{H^7CCH^6}$ 8.4, $^4J_{H^8CCCH^6}$ 0.9, $^4J_{POCCH^6}$ 0.9, $^5J_{H^9CCCCH^6}$ 0.4); 4.49 d.q (OCH_2, 2H, $^3J_{POCH}$ 12.1, $^3J_{FC}DC_H$ 7.7). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm (*J*, Hz): –75.79 br.t.m (CH_2CF_3, $^3J_{HCCF}$ 7.8), –64.93 br.s (CF_3, 6F). ^{31}P NMR spectrum (162.0 MHz, CH_2Cl_3), δ_P, ppm (*J*, Hz): –54.5 t ($^3J_{POCH}$ 12.2). Found, %: C 34.17; H 1.53. $C_{13}H_6F_9O_6P$. Calculated, %: C 33.91; H 1.30. Compound **IIc** was heated in toluene (110°C) for 8 h, after which the solvent was removed in a vacuum (12 mm), and the residue was distilled in a vacuum to obtain 4,5-bis(trifluoromethyl)-2-(2,2,2-trifluoroethoxy)-1,3,2λ^5-dioxaphosphole 2-oxide **VIIc**, yield 27%, bp 80°C (0.2 mm Hg). ^1H NMR spectrum (300 MHz, $CDCl_3$ + 10% CH_2Cl_2), δ, ppm (*J*, Hz): 4.69 d.q ($^3J_{POCH}$ 12.1, $^3J_{FCCH}$ 7.8). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm (*J*, Hz): –64.93 br.s (CF_3), –75.78 t ($^3J_{FCCH}$ 7.8). ^{31}P NMR spectrum (121.43 MHz, CH_2Cl_2), δ_P, ppm: 9.7 br.t ($^3J_{POCH}$ 12.1 Hz). Found, %: C 21.33; H 1.03. $C_6H_2F_9O_4P$. Calculated, %: C 21.18; H 0.59.

Reaction of 2-(2,2,3,3-tetrafluoropropoxy)benzo[*e*][1,3,2]dioxaphosphinin-4-one (Id) with perfluorodiacetyl. To a solution of 7.4 g of phosphinine **Id** in 15 ml of CH_2Cl_2, a solution of 4.81 g of perfluorodiacetyl in 6 ml of CH_2Cl_2 was slowly added dropwise with stirring at –25°C under argon. The reaction mixture was allowed to stand for 1 day at room temperature. The crystals that formed were filtered off and dried in a vacuum (12 mm Hg) to obtain 4',5'-bis(trifluoromethyl)-4-oxo-2-(2,2,3,3-tetrafluoropropoxy)-2λ^5-spiro[benzo[*e*][1,3,2]dioxaphosphinine-2,2'-[1,3,2]dioxaphosphole] (**IId**), yield 95%, mp 78°C. IR spectrum, ν, cm^{-1}: 1756, 1732 sh., 1700, 1668, 1620, 1595, 1323, 1308, 1212, 1075, 1060, 1030, 1000, 975, 950, 900. ^1H NMR spectrum (300 MHz), δ, ppm (*J*, Hz): 8.05 d.d (H^9, 1H, $^3J_{H^8CCH^9}$ 7.8, $^4J_{H^7CCCH^9}$ 1.7); 7.72 d.d.d.d (H^7, 1H, $^3J_{H^6CCH^7}$ 8.4, $^3J_{H^8CCH^7}$ 7.8, $^4J_{H^9CCCH^7}$ 1.7, $^5J_{POCCCH^7}$ 2.2); 7.72 d.d.d.d (H^7, 1H, $^3J_{H^6CCH^7}$ 8.4, $^3J_{H^8CCH^7}$ 2.20); 7.36 d.d.d (H^8, ^1H, $^3J_{H^7CCH^8}$ 7.8, $^3J_{H^9CCH^8}$ 7.8, $^4J_{H^6CCCH^8}$ 0.9); 7.25 br.d (H^6, ^1H, $^3J_{H^7CCH^6}$ 8.4); 5.80 t.t (CHF_2, 1H, $^2J_{FCCH}$ 3.6); 4.54 br.d.t (CH_2, 2H, $^3J_{FCCH}$ 12.3, $^3J_{POCH}$ 12.2). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm (*J*, Hz): –65.51 br.s (CF_3, 6F), –138.44 d (CHF_2, 2F, $^2J_{HF}$ 53.0), –125.66 br.t (CF_2, 2F, $^3J_{HF}$ 12.2). ^{31}P NMR spectrum (162.0 MHz, CH_2Cl_2), δ_P, ppm (*J*, Hz): –55.1 br.t ($^3J_{POCH}$ 12.1). Found, %: C 34.21; H 1.67. $C_{14}H_7F_{10}O_6P$. Calculated, %: C 34.15; H 1.42.

Reaction of 2-phenylbenzo[*e*][1,3,2]dioxaphosphinin-4-one (Ie) with perfluorodiacetyl. To a solution of 6.27 g of phosphinine **Ie** in 20 ml of CH_2Cl_2, 4.98 g of perfluorodiacetyl in 5 ml of methylene chloride was slowly added at –25°C under argon. The reaction mixture was let to warm up to 15–20°C, and the solvent was removed in a vacuum (12 mm Hg) at a temperature of no higher than 15°C. The resulting viscous colorless oil, 4',5'-bis(trifluoromethyl)-4-oxo-2-phenyl-2λ^5-spiro[benzo[*e*][1,3,2]dioxaphosphinine-2,2'-[1,3,2]dioxaphosphole] (yield 90%) is thermally and hydrolytically unstable. IR spectrum, ν, cm^{-1}: 1784, 1747 sh., 1682, 1614, 1594, 1481, 1465, 1453, 1355, 1219, 1171, 1132, 11.06, 995, 934, 774, 751, 691. ^{19}F NMR spectrum (CH_2Cl_2), δ_F, ppm: –64.93 br.s. ^{31}P–{^1H} NMR spectrum (121.42 MHz, $CDCl_3$), δ_P, ppm: –34.1 ppm. After heating in $CHCl_3$ for 6 days at 68°C, the content of phosphorane **IIe** decreases to 61.2%. Under these conditions, 27% of 2-phenyl-4-(trifluoroacetyl)-4-(trifluoromethyl)-4,5-dihydrobenzo[*f*][1,3,2λ^5]dioxaphosphepin-5-one 2-oxides (**IXe**) formed. ^{31}P NMR spectrum of compound **VIIe** (CH_2Cl_2), δ, ppm (*J*, Hz): 19.1 br.t ($^3J_{FCCH}$ 14.8). ^{31}P NMR spectrum of compound **IXe**, δ_P, ppm (*J*, Hz): 15.1 and 12.8 br.m (7 : 6). ^{19}F NMR spectrum (CH_2Cl_2) of compound **IXe**, δ_F, ppm: –61.26 br.s, –67.43 br.s. Attempted distillation of the mixture of compounds **VIIe** and **IXe** failed because of tarring.

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