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Dedicated to the 90th Anniversary of Corresponding Member of the Russian Academy of Sciences A.N. Pudovik

Preparation and Steric Structure of 2-Alkoxy-2,5-dioxo-4,4-bis(trifluoromethyl)-7(8)-chloro-1,3,2λ^5-benzodioxaphosphepins. Effect of Fluorinated Fragments on the Crystal Packing

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Abstract—The reaction of hexafluoroacetone with 2-alkoxy-6(7)-chloro-1,3,2-benzodioxaphosphorin-4-ones yielded 7- and 8-chloro-substituted 2-alkoxy-2,5-dioxo-4,4-bis(trifluoromethyl)-1,3,2λ^5-benzodioxaphosphepines. Their steric structure was studied by single-crystal X-ray diffraction. The effect of fluorinated substituents on the crystal packing of the benzophosphepines was demonstrated. Hydrolysis of these compounds gave the corresponding 4- and 5-chloro-substituted 2-(2-hydroxyphenyl)-2-oxo-1,1-bis(trifluoromethyl)-ethanols; the structure of 2-(2-hydroxy-5-chlorophenyl)-2-oxo-1,1-bis(trifluoromethyl)ethanol was also proved by single-crystal X-ray diffraction.

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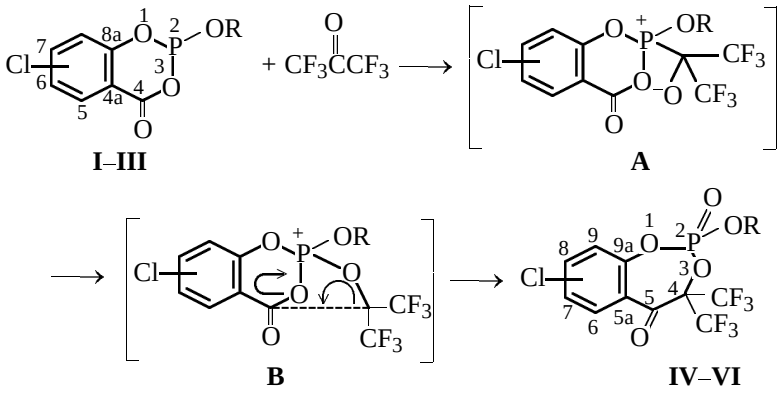
Phosphorylated derivatives of salicylic acid, 2-R-5(6)-chloro-1,3,2-benzodioxaphosphinin-4-ones (salicyl phosphites) containing the reactive macroergic fragment P–O–C(O), when treated with active carbonyl compounds, readily undergo ring expansion or opening (depending on the reagent structure) to form heterocyclic (1,3,2- and 1,4,2-dioxaphosphepines, spirophosphoranes) and open-chain (phosphates) products [1–4].

We found previously that, with 2-R-1,3,2-benzodioxaphosphinin-4-ones unsubstituted in the benzo moiety, hexafluoroacetone forms exclusively the ring expansion products, seven-membered benzo-1,3,2-dioxaphosphepines [5–8].

In this paper, which continues our previous studies [5, 6, 8], we show that salicyl phosphites **I**–**III** Cl-substituted in the benzo moiety also form benzo-1,3,2-dioxaphosphepines **IV**–**VI** under mild conditions. The starting compounds were prepared by reactions of the corresponding alcohols with 2,6(7)-dichloro-1,3,2-benzodioxaphosphinin-4-ones in the presence of triethylamine. Their structures were proved by NMR spectroscopy and high-resolution mass spectrometry. The reactions were performed in CCl_4; hexafluoroacetone was condensed into the reaction mixture at –50°C, which was followed by slow warming to 0°C. Compounds **IV** and **VI** are crystalline, and **V** is a viscous liquid.

The structures of **IV**–**VI** were proved by ^{1}H, ^{13}C, ^{19}F, and ^{31}P NMR and IR spectroscopy (see Experimental). In the ^{31}P–{^{1}H} NMR spectrum, phosphepine **VI** gives a signal at δ_P –10.5 ppm, and in the ^{19}F NMR spectrum the trifluoromethyl groups give an A_3B_3 pattern with δ_F –72.38 and –72.73 ppm ($^4J_{FF}$ 9.4 Hz). In the ^{1}H NMR spectrum (δ, ppm, *J*, Hz), the methoxyl protons give a doublet at δ 4.10 ($^3J_{POCH}$ 11.9); the benzo fragment gives a typical three-spin pattern ($H^6H^7H^9$) [δ 7.31 br.d.d (H^9, $^4J_{PH^9}$ 1.5, $^4J_{H^7H^9}$ 1.9), 7.41 d.d.d (H^7, $^3J_{H^6H^7}$ 8.5, $^4J_{H^9H^7}$ 1.9, $^6J_{PH^7}$ 0.7), 7.73 br.d (H^6, $^3J_{H^7H^6}$ 8.5)]. The ^{13}C–{^{1}H} spectrum (see Experimental) contains signals characteristic of the C^5(O)–C^4–O–P fragment [δ_C 183.95 s (C^5) and 82.96 sept.d (C^4)].

We believe that the reaction starts with the nucleophilic attack of the P atom at the electrophilic C atom of hexafluoroacetone with the formation of dipolar ion **A** with a P–C bond, which subsequently rearranges



R = Me, 6-Cl (**I**; $OCH_2CF_2CHF_2$ (**II**); Me, 7-Cl (**III**); Me, 7-Cl (**IV**); $OCH_2CF_2CHF_2$, 7-Cl (**V**); Me, 8-Cl (**VI**).

into ion **B** with a P–OC bond. Dipolar ion **B** is stabilized by intramolecular nucleophilic attack of the carbanionic center at the C atom of the endocyclic C=O group to form phosphepines **IV**–**VI**.

The structures of **IV** and **VI** were confirmed by single-crystal X-ray diffraction. Compound **IV** forms monoclinic crystals with one independent molecule in the asymmetric part of the unit cell (Fig. 1). The selected geometric parameters of **IV** are given in Table 1. The conformation of the seven-membered ring of **IV** is a distorted *boat*. The heteroring has a planar (within 0.001 Å) tetraatomic fragment C^1C^{9a}. $C^{5a}C^5$ annelated with the benzene ring; the P^2, O^3, and C^4 atoms deviate from this plane to the same side but by different distances: 1.3220(8), 1.771(2), and 0.987(3) Å, respectively. The phosphoryl group is in the pseudoequatorial position, and the methoxy group, in the pseudoaxial position. The P^2–O^1 and P^2–O^3 bond lengths have typical values. The P=O bond length is somewhat smaller than the statistical average value for equatorial P=O groups. The endocyclic angle at the P atom is 103.41(9)°.

In the crystal of **IV**, there are intermolecular hydrogen bonds of type C–H···O. The molecules in the crystal are combined by C^6–H^6···$O^{2'}$ and C^{12}–H^{122}···$O^{5''}$ hydrogen bonds in infinite layers parallel to the *a*0*c* crystallographic plane (Fig. 2); each molecule participates in a pair of such interactions as both a donor and an acceptor. The parameters of the hydrogen bonds are as follows: C^6–H^6···$O^{2'}$ (*x*, 1/2 – *y*, –1/2 + *z*), *d*(H^6···$O^{2'}$) 2.61(2) Å, ∠C^6–H^6···$O^{2'}$ 146(1)°; C^{12}–H^{122}···$O^{5''}$ (1 + *x*, 1/2 – *y*, 1/2 + *z*), *d*(H^{122}···$O^{5''}$) 2.50(3) Å, ∠C^{12}–H^{122}···$O^{5''}$ 112(2)°.

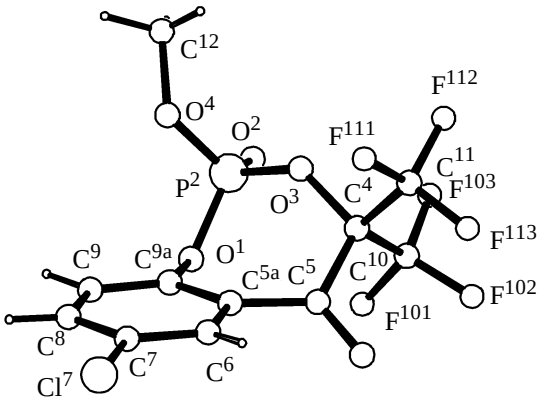


Fig. 1. Geometry of the molecule of **IV** in crystal.

The crystal packing is characterized by parallel packing of the molecular layers along the 0b direction in the crystal; the mutual arrangement of the annelated benzene rings in the adjacent layers favors the attractive dispersion interaction between these aromatic fragments. The parameters of this interaction are as follows: with the molecule related by the symmetry center (symmetry code –*x*, –*y*, –*z*), distance between the ring centers 3.84 Å, dihedral angle between the ring planes 0°, the shortest distance between the ring planes 3.39 Å; with the molecule related by the other center (symmetry code 1 – *x*, –*y*, –*z*), distance between the ring centers 4.45 Å, dihedral angle between the ring planes 0°, the shortest distance between the ring planes 3.31 Å. All these characteristics are indicative of the stacking effect in the crystal (formation of molecular stacks aronge the 0*a* axis of the crystal, Fig. 3). The crystal packing coefficient [5] is as high as 68.7%. An interesting feature is localization of regions with fluorinated fragments, with the shortest F···F distance of 3.138(3) Å. These fragments form supramolecular structures in the crystal in the form of infinite ellipsoidal cylinders oriented along the 0*a* crystallographic direction (Fig. 3).

The molecule of **VI** (isomer of **IV**) differs from **IV** only in the position of Cl in the annelated benzene ring; this, however, leads to major changes in the crystal structure. First, the asymmetric part of the unit

Table 1. Selected geometric parameters of **IV**: bond lengths *d*, bond angles ω, and torsion angles τ

Bond	*d*, Å	Bond	*d*, Å	Bond	*d*, Å
P^2–O^1	1.583(2)	Cl^7–C^7	1.729(2)	C^{5a}–C^{9a}	1.397(3)
P^2–O^2	1.439(2)	Cl^1–C^7	1.729(2)	O^3–C^4	1.413(3)
P^2–O^3	1.589(2)	C^4–C^5	1.559(3)	O^5–C^5	1.201(3)
P^2–O^4	1.542(2)	C^5–C^{5a}	1.487(3)	O^1–C^{9a}	1.402(3)
Angle	ω, deg	Angle	ω, deg	Angle	ω, deg
$O^1P^2O^2$	113.8(1)	$O^2P^2O^3$	114.7(1)	$P^2O^1C^{9a}$	119.9(2)
$O^1P^2O^3$	103.41(9)	$O^2P^2O^4$	118.3(1)	$P^2O^3C^4$	129.6(2)
$O^1P^2O^4$	103.7(1)	$O^3P^2O^4$	100.9(1)		
Angle	τ, deg	Angle	τ, deg	Angle	τ, deg
$O^2P^2O^1C^{9a}$	176.3(2)	$O^4P^2O^3C^4$	148.6(2)	$P^2O^3C^4C^{10}$	59.5(3)
$O^3P^2O^1C^{9a}$	51.2(2)	$O^1P^2O^4C^{12}$	–159.6(2)	$P^2O^3C^4C^{11}$	179.0(2)
$O^4P^2O^1C^{9a}$	–53.8(2)	$P^2O^1C^{9a}C^{5a}$	–74.3(2)	$O^5C^5C^{5a}C^{9a}$	–136.8(2)
$O^1P^2O^3C^4$	41.5(2)	$P^2O^1C^{9a}C9$	110.1(2)	$O^5C^5C^{5a}C6$	38.0(3)
$O^2P^2O^3C^4$	–83.0(2)	$P^2O^3C^4C^5$	–65.3(3)	$C^4C^5C^{5a}C^{9a}$	47.8(3)

cell of the triclinic crystal of **VI** contains two independent molecules **A** and **B** of the phosphepine (Fig. 4) with opposite configurations of the P atom. The selected geometric parameters of these molecules are given in Table 2.

The conformation of the heterorings in independent molecules of **VI** is the same as in **IV**, a distorted *boat* with a planar [within 0.005(4) and 0.008(4) Å for molecules **A** and **B**, respectively] $O^1C^{9a}C^{5a}C^5$ fragment and the P^2, O^3, and C^4 atoms deviating to the same side by different distances [by –1.326(1), –1.787(3), and –0.982(4) Å in molecule **A** and by –1.341(1), –1.770(3), and –0.976(4) Å in molecule **B**, respectively]. The phosphoryl group is in the pseudoequatorial, and the methoxy group, in the pseudoaxial position. On the whole, the two molecules (apart from their inverse configuration) differ only slightly in the positions of substituents, as can be seen from Fig. 5.

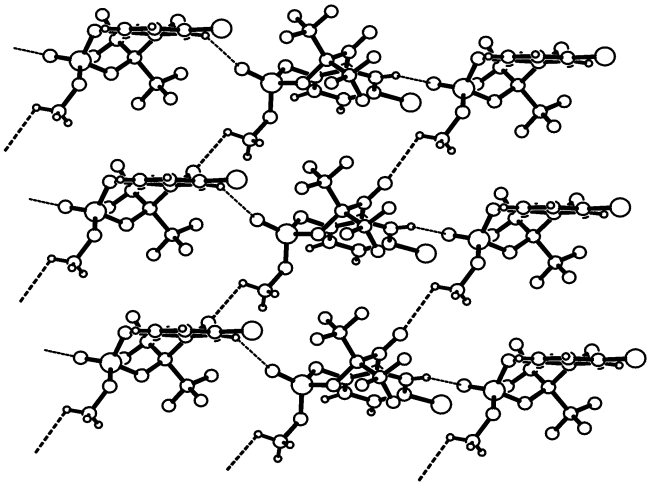


Fig. 2. Lamellar supramolecular structure in the crystal of **IV**. View along the 0*b* crystallographic axis; C–H···O bonds are shown by dashed lines.

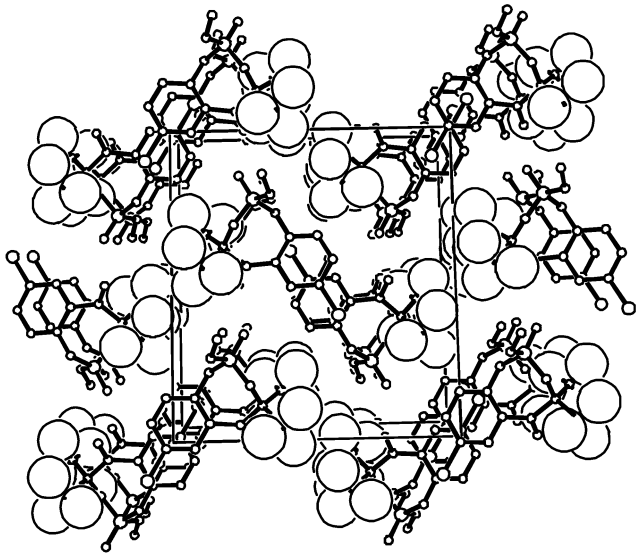


Fig. 3. Fragment of the crystal packing of **IV**. The fluorine atoms are shown as big spheres. View along the 0*a* crystallographic axis.

Table 2. Selected geometric parameters of **VI**: bond lengths *d*, bond angles ω, and torsion angles τ

Bond	*d*, Å	Bond	*d*, Å	Bond	*d*, Å
Cl^{8a}–C^{8a}	1.744(5)	P^{2a}–O^{2a}	1.443(3)	O^{5b}–C^{5b}	1.210(6)
Cl^{8b}–C^{8b}	1.744(5)	P^{2a}–O^{3a}	1.589(3)	C^{4b}–C^{5b}	1.543(6)
P^{2b}–O^{1b}	1.580(3)	P^{2a}–O^{4a}	1.537(3)	C^{4a}–C^{5a}	1.533(6)
P^{2b}–O^{2b}	1.454(3)	O^{1a}–C^{9aa}	1.414(5)	C^{5ba}–C^{5b}	1.468(6)
P^{2b}–O^{3b}	1.583(3)	O^{3b}–C^{4b}	1.415(5)	C^{5aa}–C^{5a}	1.489(6)
P^{2b}–O^{4b}	1.546(3)	O^{3a}–C^{4a}	1.425(5)		
P^{2a}–O^{1a}	1.567(3)	O^{5a}–C^{5a}	1.206(6)		
Angle	**ω, deg**	**Angle**	**ω, deg**	**Angle**	**ω, deg**
$O^{1b}P^{2b}O^{2b}$	110.0(2)	$O^{2b}P^{2b}O^{4b}$	118.5(2)	$O^{1a}P^{2a}O^{4a}$	106.7(2)
$O^{1b}P^{2b}O^{3b}$	103.9(1)	$O^{3b}P^{2b}O^{4b}$	97.7(2)	$O^{2a}P^{2a}O^{3a}$	117.4(2)
$O^{1b}P^{2b}O^{4b}$	107.8(2)	$O^{1a}P^{2a}O^{2a}$	111.1(2)	$O^{2a}P^{2a}O^{4a}$	119.0(2)
$O^{2b}P^{2b}O^{3b}$	117.4(2)	$O^{1a}P^{2a}O^{3a}$	103.5(2)	$O^{3a}P^{2a}O^{4a}$	97.2(2)
Angle	**τ, deg**	**Angle**	**τ, deg**	**Angle**	**τ, deg**
$O^{2b}P^{2b}O^{1b}C^{9ba}$	–179.4(3)	$O^{3b}P^{2b}O^{4b}C^{10b}$	161.3(3)	$O^{2a}P^{2a}O^{4a}C^{10a}$	15.2(5)
$O^{3b}P^{2b}O^{1b}C^{9ba}$	54.1(3)	$O^{2a}P^{2a}O^{1a}C^{9aa}$	179.4(3)	$O^{3a}P^{2a}O^{4a}C^{10a}$	142.1(4)
$O^{4b}P^{2b}O^{1b}C^{9ba}$	–48.8(3)	$O^{3a}P^{2a}O^{1a}C^{9aa}$	52.6(3)	$P^{2b}O^{3b}C^{4b}C1^{1b}$	–178.6(3)
$O^{1b}P^{2b}O^{3b}C^{4b}$	35.9(4)	$O^{4a}P^{2a}O^{1a}C^{9aa}$	–49.4(3)	$P^{2b}O^{3b}C^{4b}C1^{2b}$	62.4(5)
$O^{2b}P^{2b}O^{3b}C^{4b}$	–85.7(4)	$O^{1a}P^{2a}O^{3a}C^{4a}$	39.7(4)	$P^{2a}O^{3a}C^{4a}C1^{1a}$	179.6(3)
$O^{4b}P^{2b}O^{3b}C^{4b}$	146.4(3)	$O^{2a}P^{2a}O^{3a}C^{4a}$	–83.1(4)	$P^{2a}O^{3a}C^{4a}C1^{2a}$	60.2(5)
$O^{1b}P^{2b}O^{4b}C^{10b}$	–91.4(3)	$O^{4a}P^{2a}O^{3a}C^{4a}$	148.8(3)		
$O^{2b}P^{2b}O^{4b}C^{10b}$	34.2(4)	$O^{1a}P^{2a}O^{4a}C^{10a}$	–111.4(4)		

The system of intermolecular contacts in the crystal of **VI** differs essentially from that in **IV** and involves diverse types of contacts. The most significant of them are the following. Each of the two independent molecules forms a centrosymmetric dimer through the pair of C–H···O contacts with the following parameters: C_{9a}–H_{9a}···$O^{2a'}$ (1 – *x*, –1 – *y*, 1 – *z*), *d*(H^{9a}···$O^{2a'}$) 2.39 Å, ∠C^{9a}–H^{9a}···$O^{2a'}$ 149°; C^{9b}–H^{9b}···$O^{2b''}$ (2 – *x*, –*y*, –*z*), *d*(H^{9b}···$O^{2b''}$) 2.31 Å, ∠C^{9b}–H^{9b}···$O^{2b''}$ 166° (Fig. 6). Participation of the $O^{2b'''}$ atoms in a bifurcate hydrogen bond with the H^{6a} proton of the annelated benzene ring [*d*(H^{6a}···$O^{2b'''}$) 2.42 Å, ∠C^{6a}–

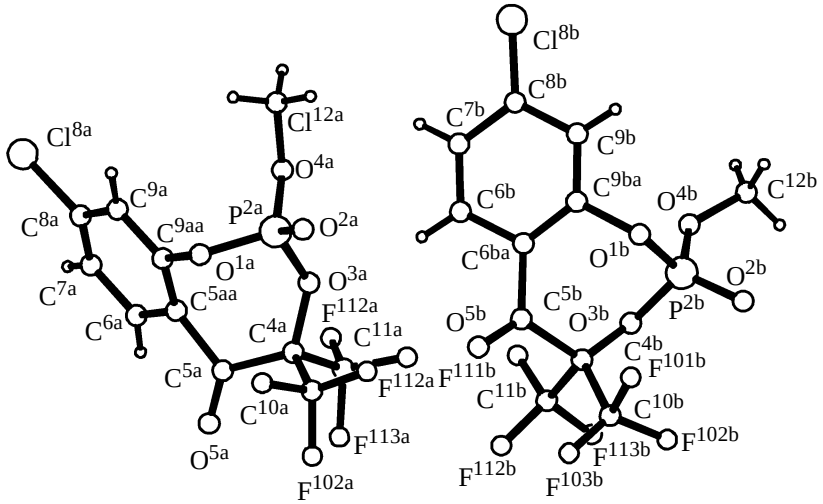
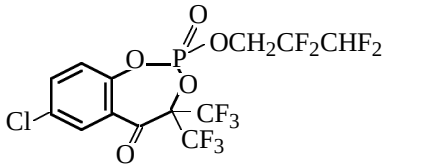


Fig. 4. Geometry of two independent molecules of **VI** in crystal.

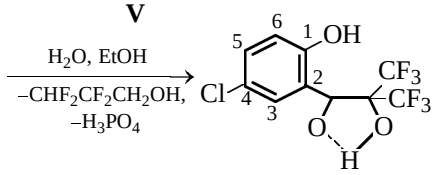
$H^{6a}\cdots O^{2b'''}$ 138°, (1 – *x*, –y, 1 – *z*)] links the dimers in a chain oriented along the diagonal of the 0*bc* plane.

The molecular packing in crystal of **VI** is characterized by the absence of the π–π contacts; however, similarly to the structure of **IV**, the fluorinated fragments are localized in definite regions, and the intermolecular distances F···F range from 2.945(5) to 3.044(4) Å, i.e., are somewhat shorter than those in **IV**. The number of such contacts is appreciably larger than in **IV**. The morphological type of the supramolecular structure formed by the CF_3 groups is the same as in **IV** (infinite cylinders oriented along the 0*a* axis), but the cross section of these cylinders is appreciably larger (Fig. 7). The packing coefficient in **VI** is somewhat lower (68.3%) than in **IV**, despite considerably larger number and diversity of short intermolecular contacts; this fact once again demonstrates the lack of correlation between the extent of intermolecular interaction and packing density. The larger packing coefficient in **IV** indicates that the location of Cl in the 8-position of the annelated benzene ring is more favorable for the crystal packing.

We also performed the hydrolysis of **V** in aqueous alcohol on heating (60°C). By vacuum distillation we isolated lemon-yellow crystals of fluorinated hydroxo ketone **VII**.



V



VII

The ^{19}F NMR spectrum ($CDCl_3$) of this compound contains a signal with δ_F –73.30 ppm, which is characteristic of the CF_3 group. In the IR spectrum, there are bands characteristic of an OH group involved in strong intramolecular (chelating) hydrogen bonding (ν 3032–3288 cm^{-1}) and of a C=O group in a fluorinatde ketone (ν 1648 cm^{-1}). The presence of two different OH signals in the ^1H NMR spectrum of **VII** (δ 11.21 and 5.05 ppm) indicates that only one of the two OH groups (giving the lower-field signal) is hydrogen-bonded and that the exchange is slow (otherwise an averaged signal would be observed). This pattern is consistent with the structure of 2-(2'-hydroxy-5'-chlorophenyl)-2-oxo-1,1-bis(trifluoromethyl)ethanol

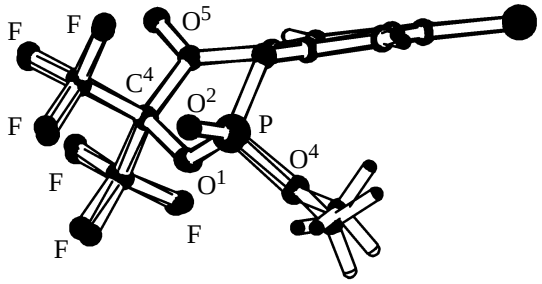


Fig. 5. Superposition of independent molecules **A** and **B** (inverted) of **VI**.

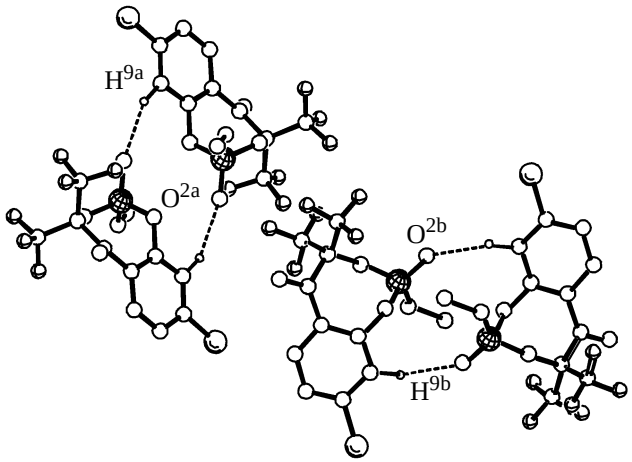


Fig. 6. Formation of centrosymmetric dimers from independent molecules of **VI** by C–H···O hydrogen bonding (dashed lines).

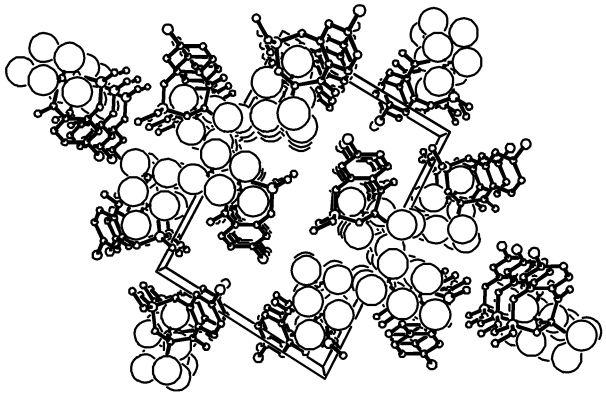


Fig. 7. Fragment of molecular packing of **VI** in crystal. Fluorine atoms are shown as big spheres. View along the 0*a* crystallographic axis.

VII and is close to that observed with the previously synthesized 2-(2'-hydroxyphenyl)-2-oxo-1,1-bis(trifluoromethyl)ethanol [9].

The structure of **VII** was also confirmed by single crystal X-ray diffraction. Compound **VII** crystallizes in the rhombic system with one molecule in the asym-

Table 3. Selected geometric parameters of **VII:** bond lengths *d*, bond angles ω, and torsion angles τ

Bond	*d*, Å	Bond	*d*, Å	Bond	*d*, Å
Cl^4–C^4	1.730(5)	C^2–C^3	1.399(6)	O^8–C^8	1.385(5)
C^1–C^2	1.413(6)	O^1–C^1	1.346(5)	C^8–C^9	1.533(7)
C^5–C^6	1.358(7)	C^2–C^7	1.464(6)	C^8–C^{10}	1.542(7)
C^4–C^5	1.392(7)	O^7–C^7	1.221(6)	C^1–C^2	1.384(7)
C^3–C^4	1.350(6)	C^7–C^8	1.540(6)		
Angle	ω, deg	Angle	ω, deg	Angle	ω, deg
$O^1C^1C^2$	122.6(4)	$C^2C^7C^8$	124.1(4)	$O^8C^8C^7$	110.9(4)
$O^1C^1C^6$	117.2(4)	$C^9C^8C^{10}$	113.0(4)		
Angle	τ, deg	Angle	τ, deg	Angle	τ, deg
$O^1C^1C^2C^7$	2.4(7)	$C^2C^7C^8O^8$	–19.2(6)	$C^1C^2C^7O^7$	–15.0(7)

metric part of the unit cell (Fig. 8). The selected geometric parameters of the molecule of **VII** are given in Table 3. The bond lengths have typical values. The trifluoromethyl groups at the C^8 atom are in the *gauche* conformation relative to each other and are arranged above and below the benzene ring plane.

In the crystal, the proton of the O^1–H^1 group is involved in intramolecular hydrogen bond with the carboxyl oxygen atom O^7. The parameters of the H bond are as follows: $d(H^1\cdots O^7)$ 2.03(3) Å, $\angle O^1$–$H^1\cdots O^7$ 132(3)°.

The molecular packing in the crystal is determined by classical hydrogen bonds O–H···O and π–π intercations between the electronic systems of the aromatic rings (Fig. 9). The molecules are linked by the O^8–$H^8\cdots O^{1'}$ (x, 1 – y, –1/2 + z) hydrogen bond in infinite chains oriented along the 0z crystallographic axis. The parameters of the H bond are as follows: $d(H^8\cdots O^{1'})$ 1.76(3) Å, $\angle O^8$–$H^8\cdots O^{1'}$ 169(3)°. The annelated benzene fragments of molecules in a chain form π–π contacts with the benzene rings of the centrosymmetrical molecules of an antiparallel chain; the distances between the ring centers are 3.86(1) Å, the dihedral angles between the ring planes are 0°, the shortest distances between the ring planes are 3.53 Å, and the angles between the normal to the ring plane and the line connecting the ring centers are 23.9°.

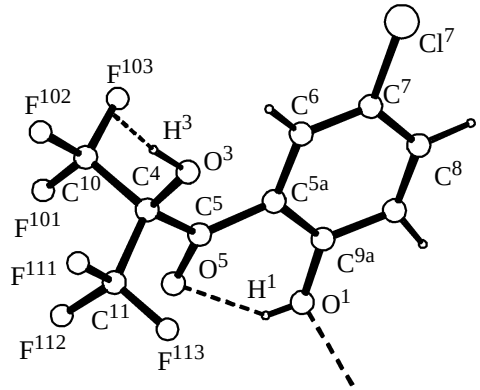


Fig. 8. Molecular geometry of **VII** in crystal.

In the crystal, these supramolecular structures are arranged parallel to each other, forming a relatively dense packing (packing coefficient 68.4%). The fluorinated fragments in this molecule are also localized; the F···F distances are within 3.034–3.065 Å. How-

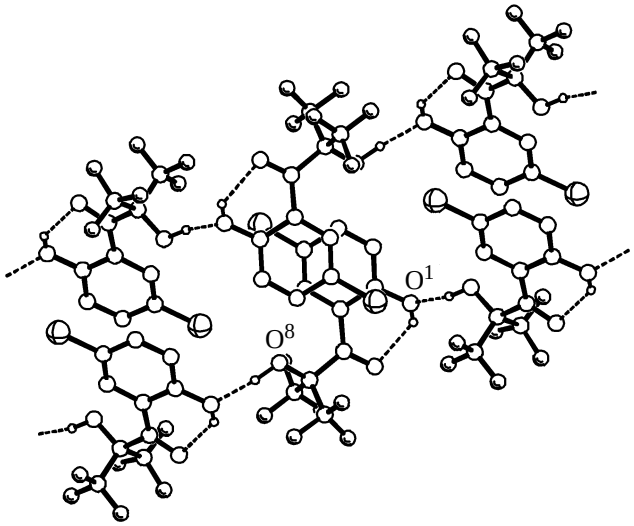


Fig. 9. Fragment of the supramolecular structure of **VII** in crystal. The O–H···O bonds are shown by dashed lines.

ever, the type of associaties of the CF_3 groups is different. Presumably, the morphological type of such associates will depend on the fraction occupied by fluorinated fragments in the total molecular volume and on the ratio of the volume fractions of hydrophilic and hydrophobic fragments of the molecule [10–13]. As the absence of the phosphorus-containing fragment in **VII** results not only in its lower molecular weight and smaller molecular volume, but also in the larger volume fraction of the fluorinated fragments, it can be expected that the cylindrical morphology observed in **IV** and **VI** will give way to another pattern in **VII**. Indeed, in the structure of **VII** the pattern is inverse: fluorinated fragments form a continuous matrix, and hydrocarbon fragments form cylindrical associates in this matrix (Fig. 10).

The whole set of data on the crystal structure of **IV**, **VI**, and **VII** indicates that the type of the supramolecular structure in the crystal largely depends not only on the types of intermolecular interactions realized, but also on localization of halogen-containing fragments; the morphological structure depends on the fraction of these fragments in the total molecular volume [14]. The position of the substituent (Cl) in the annelated benzene ring (for **IV** and **VI**) does not alter this ratio (and hence the morphological type of supramolecular structures) but affects the mutual arrangement of molecules in the crystal, the crystal packing, and even the crystal symmetry.

Thus, 2-alkoxy-1,3,2-benzodioxaphosphinin-4-ones Cl-substituted in the benzo fragment also react with hexafluoroacetone to form 1,3,2-benzodioxaphosphepines; this is the general route to these seven-membered heterocycles whose hydrolysis allows preparation of difficultly accessible fluorinated hydroxy ketones.

EXPERIMENTAL

The IR spectra were recorded on a Specord M-80 spectrometer from thin films or mulls in mineral oil between KBr plates. The NMR spectra were taken on a Varian Unity-300 spectrometer (^{1}H, 300 MHz; ^{31}P, 121.421 MHz; ^{19}F, 287.2 MHz) in $CDCl_3$. The ^{13}C and ^{13}C–{^{1}H} NMR spectra were recorded on a Bruker MSL-400 spectrometer (100.6 MHz, $CDCl_3$). The ^{1}H and ^{13}C chemical shifts were calculated relative to TMS. For ^{19}F, the internal reference was C_6F_6, and the chemical shifts were recalculated relative to $CFCl_3$. The electron impact (70 eV) mass spectra were taken on a TRACE-MS Finnigan-MAT device at an ion source temperature of 200°C. The conditions of X-ray diffraction analysis are given in Table 4.

2,6-Dichloro-1,3,2-benzodioxaphosphinin-4-one. A mixture of 50 g of 5-chlorosalicylic acid in 350 ml of toluene and excess PCl_3 (32 ml) was heated for 3 h at 110°C with continuous stirring until the HCl evolution ceased. The precipitate that formed after standing at 20°C for 12 h was filtered off; the solvent was distilled off, and the residue (50 ml) was again allowed to stand at 20°C. The precipitate thus formed was combined with the first portion of the precipitate and vacuum-dried (12 mm Hg). 2,6-Dichloro-1,3,2-benzodioxaphosphinin-4-one was isolated in 53% yield, bp 138°C (0.1 mm Hg), mp 63°C. ^{31}P–{^{1}H} NMR spectrum (CH_2Cl_2): δ_P 165 ppm.

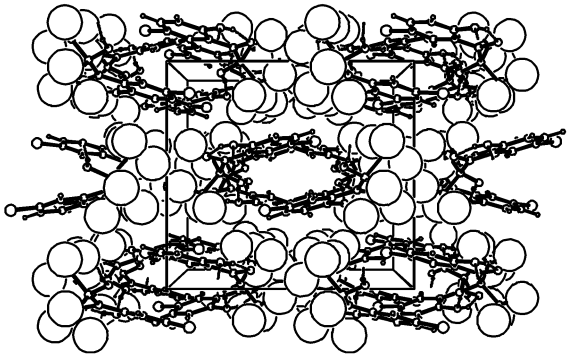


Fig. 10. Fragment of molecular packing of **VII** in crystal. Fluorine atoms are shown as big spheres. View along the 0*a* crystallographic axis.

2,7-Dichloro-1,3,2-benzodioxaphosphinin-4-one. A mixture of 30 g of 4-chlorosalicylic acid in 200 ml of toluene and excess PCl_3 (18.9 ml) was heated for 3 h at 110°C with continuous stirring until the HCl evolution ceased. The precipitate that formed after standing at 20°C for 12 h was filtered off; the solvent was distilled off, and the residue (50 ml) was again allowed to stand at 20°C. The precipitate thus formed was combined with the first portion of the precipitate and vacuum-dried (12 mm Hg). 2,7-Dichloro-1,3,2-benzodioxaphosphinin-4-one was isolated in 63% yield; bp 100°C (0.2 mm Hg), mp 60°C. ^{31}P–{^{1}H} NMR spectrum (CH_2Cl_2): δ_P 150.0 ppm.

2-Methoxy-6-chloro-1,3,2-benzodioxaphosphinin-4-one (I). A mixture of 5.5 ml of methanol and 19 ml of triethylamine, diluted twofold with ether, was added dropwise with stirring at –20°C under dry Ar to 32.49 g of 2,6-dichloro-1,3,2-benzodioxaphosphinin-4-one in 250 ml of anhydrous ether. The mixture was stirred until it warmed up to room temperature. The precipitate was filtered off, and the solvent was removed. 1,3,2-Dioxaphosphinin-4-one **I** was obtained in 52% yield, bp 102–104°C (0.02 mm Hg), n_D^{20} 1.4807. IR spectrum, ν, cm^{-1}: 1740, 1608, 1472, 1415, 1376, 1276, 1156, 1096, 1024, 944, 896, 832,

Table 4. Parameters of the crystals of **IV, VI**, and **VII** and conditions of X-ray diffraction experiments[a]

Parameter	**IV**[b]	**V**[b]	**VII**[b]
Color, habit	Colorless, prismatic		Yellow, prismatic
Crystal system	Monoclinic	Triclinic	Rhombic
Space group	$P2_1/c$	$P\bar{1}$	*Pbcn*
Unit cell parameters	*a* 6.883(1), *b* 13.864(2), *c* 15.356(2) Å, β 99.70(1)°	*a* 6.674(1), *b* 12.711(4), *c* 17.622(6) Å; α 84.80(4)°, β 84.05(2)°, γ 83.15(3)°	*a* 13.497(3), *b* 12.448(4), *c* 14.167(6) Å
Volume, Å^3	1444.8(3)	1471.5(8)	2380(3)
Z	4	4	8
M	398.58	398.58	322.59
d_{calc}, g cm^{-3}	1.83	1.80	1.80
Absorption coefficient, cm^{-1}	4.61	43.00	3.99
F(000)	792	396	1280
Radiation (λ, Å)	MoK_α, λ 0.71073	CuK_α, λ 1.54184	MoK_α, λ 0.71073
Range of θ, deg	2.12 ≤ θ ≤ 27.4	3.16 ≤ θ ≤ 74.33	2.12 ≤ θ ≤ 27.4
Reference reflections	Two reflections for orientation check and three reflections for intensity check after collection of every 200 reflections		
Range of indices measured	–8 ≤ *h* ≤ 8, –17 ≤ *k* ≤ 0, –19 ≤ *l* ≤ 0	–6 ≤ *h* ≤ 0, –13 ≤ *k* ≤ 12, –17 ≤ *l* ≤ 17	–15 ≤ *h* ≤ 13, –15 ≤ *k* ≤ 14, 0 ≤ *l* ≤ 16
Number of reflections measured	2719	3945	4003
Number of observed reflections with $I > 3\sigma(I)$	1672	3219	1459
Correction for absorption	No	Yes	No
Setting and refinement of hydrogen atoms	Revealed from differential series, refined isotropically	Revealed from differential series; contribution to structural amplitudes taken into account with fixed positional and thermal parameters	Revealed from differential series, refined isotropically
Final divergence factors	*R* 0.035, R_W 0.043	*R* 0.051, R_W 0.064	*R* 0.061, R_W 0.071
Fitting parameter	1.391	2.335	2.110
Number of refined parameters	241	433	201
Number of unique reflections	1622	2960	1551

[a] Enraf–Nonius CAD-4 diffractometer; ω/2θ scanning; variable scanning rate 1–16.5 deg min^{-1} for θ; MolEN program package [15].

[b] The structure was solved by the direct method (SIR program [16]) and refined by the full-matrix least-squares method; minimized function $\Sigma(|F_{exp}| - |F_{calc}|)^2$; extinction was not taken into account; weight scheme $4F^2_{exp}/[\sigma(I)^2 + (0.04F^2_{exp})]^2$. The intermolecular contacts (including hydrogen bonds in crystals) were analyzed using the PLATON program [17].

784, 720. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 3.60 d (OCH_3, $^3J_{PH}$ 12.0), 6.98 br.d (H^7, $^3J_{H^7H^8}$ 8.8), 7.50 d.d.d (H^8, $^3J_{H^8H^7}$ 8.8, $^4J_{H^5H^7}$ 2.7, $^4J_{PH^7}$ 0.7), 7.94 br.d (H^5, $^4J_{H^5H^7}$ 2.7). ^{31}P NMR spectrum (CH_2Cl_2), δ_P, ppm (*J*, Hz): 124.4 q ($^3J_{POCH}$ 11.4). Mass spectrum, *m/z* (I_{rel}, %) (here and hereinafter, the peaks of ions containing the most abundant isotopes are indicated): 235 (0.9), 234 (7.5), 233 (2.5), 232 (21.6) $[M]^{+\cdot}$, 203 (1.9), 202 (0.5), 201 (5.7) $[M - OCH_3]^+$, 175 (1.2), 174 (0.4), 173 (3.5), 172 (0.4), 157 (5.4), 156 (35.0), 155 (10.5), 154 (100.0), 129 (3.2), 128 (37.9), 127 (9.3), 126 (91.8), 101 (1.4), 100 (13.3), 99 (6.7) 98 (40.3), 77 (21.6), 74 (31.0), 64

(11.9), 63 (88.0), 62 (65.6), 47 (83.5) $[PO]^+$, 31 (29.8) $[OCH_3]^+$.

2-(2,2,3,3-Tetrafluoropropoxy)-6-chloro-1,3,2-benzodioxaphosphinin-4-one II was prepared similarly from 13 g of 2,6-dichlorobenzo-1,3,2-dioxaphosphorin-4-one, 7.24 g of 2,2,3,3-tetrafluoropropanol, and 7.61 ml of triethylamine; yield 48%, bp 112–114°C (0.02 mm Hg), n_D^{20} 1.5538. IR spectrum, cm^{-1}: 1748, 1608, 1472, 1440, 1416, 1364, 1272, 1248, 1228, 1192, 1132, 992, 864, 836, 800, 740. ^1H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 4.26 t.d.t (CH_2, $^3J_{FCCH}$ 12.7, $^3J_{POCH}$ 11.0, $^4J_{FCCCH}$ 1.5, $^4J_{HCCCH}$ 1.5); 5.72 t.t (CHF_2, $^2J_{FCH}$ 53.1, $^3J_{FCCH}$ 4.0); 7.02 d.d (H^9, $^4J_{PH^9}$ 1.5, $^3J_{H^9H^8}$ 8.8), 7.54 d.d.d (H^8, $^3J_{H^9H^8}$ 8.8, $^4J_{H^6H^8}$ 2.6, $^5J_{POCCCH^8}$ 1.2), 7.95 d.d (H^6, $^4J_{H^8H^6}$ 2.6, $^5J_{POCCCH^6}$ 1.8). ^{31}P NMR spectrum (CH_2Cl_2), δ_P, ppm (J, Hz): 125.3 t.t ($^3J_{POCH}$ 10.9, $^4J_{FCCOP}$ 7.6). Mass spectrum, *m/z* (I_{rel}, %) 335 (0.2), 334 (0.9), 333 (0.5), 332 (2.7) $[M]^{+\cdot}$, 221 (2.2), 220 (14.7), 219 (7.1), 218 (43.5), 203 (2.3), 201 (5.5) $[M - OCH_2CF_2CHCF_2]^+$, 175 (4.6), 174 (12.6), 173 (9.2), 172 (26.8), 157 (10.6), 156 (32.8), 155 (12.8), 154 (100.0), 129 (5.8), 128 (14.8), 127 (8.1), 126 (41.1), 101 (3.3), 100 (5.1), 99 (8.7), 98 (17.7), 97 (15.2), 77 (5.2), 74 (2.8), 73 (12.7), 65 (60.6), 64 (34.3), 63 (38.0), 62 (6.1), 45 (12.1), 47 (57.5) $[PO]^+$, 31 (8.6).

2-Methoxy-7-chloro-1,3,2-benzodioxaphosphinin-4-one III. A mixture of 4.3 ml of methanol and 15 ml of triethylamine, diluted twofold with ether, was added dropwise with stirring at –20°C under dry Ar to 25.83 g of 2,7-dichloro-1,3,2-benzodioxaphosphinin-4-one in 250 ml of anhydrous ether. The mixture was stirred until it warmed up to room temperature. The precipitate was filtered off, and the solvent was removed. 1,3,2-Dioxaphosphinin-4-one **III** was obtained in 55% yield, bp 102°C (0.02 mm Hg), n_D^{20} 1.4770. ^1H NMR spectrum (CCl_4), δ, ppm (*J*, Hz): 3.60 d (OCH_3, $^3J_{PH}$ 11.4), 6.97 br.d (H^8, $^4J_{H^6H^8}$ 1.9), 7.50 br.d.d (H^6, $^3J_{H^6H^5}$ 8.5, $^4J_{H^6H^8}$ 1.9), 7.86 br.d (H^5, $^3J_{H^5H^6}$ 8.5). ^{31}P NMR spectrum (CCl_4), δ_P, ppm (J, Hz): 126.2 q ($^3J_{POCH}$ 11.5).

Reactions of 2-alkoxy-6(7)-chloro-1,3,2-benzodioxaphosphinin-4-ones I–III with hexafluoroacetone. Hexafluoroacetone was bubbled through a solution of 0.01 mol of **I**–**III** in 30–40 ml of CCl_4 up to an uptake of 0.01 mol (monitored gravimetrically). The mixture was allowed to stand for 2–3 days at room temperature. The solvent was removed in a vacuum (3 mm Hg); the residues were 2-alkoxy-2,5-dioxo-4,4-bis(trifluoromethyl)-7(8)-chloro-1,3,2λ^5-benzodioxaphosphepines **IV**–**VI** as viscous colorless oils, which were subsequently crystallized from ether.

2-Methoxy-2,5-dioxo-4,4-bis(trifluoromethyl)-7-chloro-1,3,2λ^5-benzodioxaphosphepine (IV). Yield 86%, mp 65–67°C. IR spectrum, cm^{-1}: 3070, 2960, 2920, 2858, 1725, 1600, 1558, 1475, 1460, 1398, 1373, 1321, 1285, 1270, 1235–1242, 1221–1224, 1205, 1140, 1047–1060, 975, 958, 903, 825, 782, 782, 760, 740, 710, 676, 650, 591, 565, 535, 520, 500, 465, 445. ^1H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 4.05 d (CH_3, $^3J_{POCH}$ 11.8), 7.11 d.d (H^9, $^4J_{PH^9}$ 1.4, $^3J_{H^9H^8}$ 8.8), 7.54 d.d.d (H^8, $^3J_{H^9H^8}$ 8.8, $^4J_{H^6H^8}$ 2.5, $^5J_{POCCCH^8}$ 1.0), 7.59 d (H^6, $^4J_{H^8H^6}$ 2.5). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm (*J*, Hz): –72.76 and –73.08 (A_3B_3 system) ($^4J_{FF}$ 9.3). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm (*J*, Hz) (here and hereinafter, in parentheses is the signal muiltiplicity in the $^{13}C–\{^1H\}$ NMR spectrum): 84.10 sept.d (sept.d) (C^4, $^2J_{FCC^4}$ 30.6, $^2J_{POC^4}$ 6.0); 185.54 d.d (d) (C^5, $^3J_{POCC}$ 1.6, $^3J_{HCCC^5}$ 4.4), 129.25 m (d) (C^{5a}, $^3JP_{OCC^{5a}}$ 0.9); 132.15 d.d.d.d (d) (C^6, $^1J_{HC^6}$ 171.6, $^3J_{HC^8CC^6}$ 5.8, $^4J_{POCCC^6}$ 1.3, $^4J_{HCCCC^6}$ 1.2), 133.68 d.d.d.d (d) (C^7, $^3J_{HC^9CC^7}$ 11.1, $^2J_{HCC^7}$ 4.0, $^2J_{HCC^7}$ 4.0, $^5J_{POCCCC^7}$ 1.5), 137.50 d.d (s) (C^8, $^1J_{HC^8}$ 169.4, $^3J_{HC^6CC^8}$ 6.3), 124.49 d.d (d) (C^9, $^1J_{HC^9}$ 168.5, $^3J_{POCC^9}$ 8.1), 147.43 d.d.d.d (d) (C^{9a}, $^3J_{HCCC^{9a}}$ 11.0, $^3J_{HCCC}$*9a* 8.6, $^2J_{POC^{9a}}$ 6.9, $^2J_{HC^9C^{9a}}$ 4.3), 120.59 q.d.q (CF_3, $^1J_{FC}$ 289.9, $^2J_{POC}$ 9.8, $^3J_{FCCC}$ 0.9–1.2), 120.55 q.d.q (CF_3, $^1J_{FC}$ 289.7, $^2J_{POC}$ 7.5, $^3J_{FCCC}$ 1.6), 57.85 q.d (d) (CH_3, $^1J_{HC}$ 151.2, $^2J_{POC}$ 5.9). $^{31}P–\{^1H\}$ NMR spectrum ($CDCl_3$): δ_P –10.5 ppm. Found, %: C 32.90; H 1.54. $C_{11}H_6ClF_6O_5P$. Calculated, %: C 33.12; H 1.51.

2-(2,2,3,3-Tetrafluoropropoxy)-2,5-dioxo-4,4-bis(trifluoromethyl)-7-chloro-1,3,2λ^5-benzodioxaphosphepine (V): viscous noncrystallizable colorless liquid, yield 93%. IR spectrum, cm^{-1}: 3120, 3000, 2940, 2870, 1800, 1725, 1654, 1605, 1520, 1483, 1406, 1335, 1300, 1240–1270, 1215, 1195, 1150, 1120, 1085, 1070, 991, 970, 935, 900, 840, 805, 764, 746, 716, 690, 660, 590, 573, 533, 510, 485, 450. ^1H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 4.26 t.d.t.d (CH_2, $^3J_{FCCH}$ 12.7, $^3J_{POCH}$ 11.0, $^4J_{FCCCH}$ 1.5, $^4J_{HCCCH}$ 1.5), 5.72 t.t (CHF_2, $^2J_{FCH}$ 53.1, $^3J_{FCCH}$ 4.0), 7.02 d.d (H^9, $^4J_{PH^9}$ 1.5, $^3J_{H^9H^8}$ 8.8), 7.54 d.d.d (H^8, $^3J_{H^9H^8}$ 8.8, $^4J_{H^6H^8}$ 2.6, $^5J_{POCCCH^8}$ 1.2), 7.95 d.d (H^6, $^4J_{H^8H^6}$ 2.6, $^5J_{POCCCH^6}$ 1.8). ^{19}F NMR spectrum (CCl_4), δ_F, ppm (*J*, Hz): –72.65 and –73.279 (A_3B_3 system) (CF_3, 6F, $^4J_{FF}$ 9.5), –126.03 br.t (CF_2, 2F, $^3J_{HCCF}$ 12.0), –138.57 d (CHF_2, 2F, $^2J_{HCF}$ 52.6). $^{31}P–\{^1H\}$ NMR spectrum: δ_P –13.2 ppm. Found, %: C 32.19; H 1.11. $C_{13}H_6ClF_{10}O_5P$. Calculated, %: C 31.29; H 1.20.

2-Methoxy-2,5-dioxo-4,4-bis(trifluoromethyl)-8-chloro-1,3,2λ^5-benzodioxaphosphepine (VI). Yield 78%, mp 48–50°C. IR spectrum, cm^{-1}: 1725, 1605, 1571, 1410, 1320, 1260, 1240, 1211, 1184, 1159, 1090, 1057–1080, 990, 970, 915, 900, 860, 830, 790, 745, 725, 690, 675, 615–625, 575, 545, 510, 475, 450. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 4.10 d (CH_3, $^3J_{POCH}$ 11.9), 7.31 d.d (H^9, $^4J_{PH^9}$ 1.5, $^4J_{H^7H^9}$ 1.9), 7.41 d.d (H^7, $^3J_{H^7H^6}$ 8.5, $^4J_{H^9H^7}$ 1.9), 7.74 d (H^6, $^3J_{H^6H^7}$ 8.5). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: –72.38 and –72.73 ppm (A_3B_3 system) ($^4J_{FF}$ 9.4 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm (*J*, Hz): 82.96 sept.d (sept.d) (C^4, $^2J_{FCC^4}$ 30.9, $^2J_{POC^4}$ 6.0); 183.95 d (s) (C^5, $^3J_{HC^6CC^4}$ 3.6), 125.50 m (s) (C^{5a}); 148.21 d.d.d.d (d) (C^{9a}, $^3J_{HC^6CC^{9a}}$ 10.9, $^2J_{POC^{9a}}$ 6.7, $^2J_{HC^9C^{9a}}$ 4.8), 132.71 d (s) (C^6, $^1J_{HC^6}$ 168.6); 126.98 d.d (s) (C^7, $^1J_{HC^7}$ 171.2, $^3J_{HC^9CC^7}$ 5.3), 142.79 d.d.d (s) (C^8, $^3J_{HC^6CC^8}$ 13.4, $^2J_{HCC^8}$ 4.0, $^2J_{HCC^8}$ 3.4), 121.61 d.d (d) (C^9, $^1J_{HC^9}$ 171.5, $^3J_{POCC^9}$ 8.8), 56.60 q.d (d) (CÆ$_3$, $^1J_{HC}$ 151.1, $^2J_{POC}$ 5.8), 119.55 q.d (q.d) (CF, $^1J_{FC}$ 288.8, $^3J_{POCC}$ 7.6). ^{31}P–{^{1}H} NMR spectrum ($CDCl_3$): δ_P –10.7 ppm. Found, %: C 32.80; H 1.64. $C_{11}H_6ClF_6O_5P$. Calculated, %: C 33.12; H 1.51.

Hydrolysis of phosphepine V. A 10-ml portion of aqueous ethanol (1 : 1) was added to 4.62 g of phosphepine **V**. The mixture was heated at 60°C for 4 h, cooled, and extracted with ether; the extract was dried over $MgSO_4$. After removal of the ether and vacuum sublimation of the residue, lemon-yellow crystals of 2-(2-hydroxy-5-chlorophenyl)-2-oxo-1,1-bis(trifluoromethyl)ethanol **VII** were obtained; yield 78%, mp 84%. IR spectrum, cm^{-1}: 3032–3288, 1616, 1648, 1588, 1468, 1200–1300. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 11.21 and 5.05 two br.s (OH); 8.33 br.d (H^3, $^4J_{H^5CCCH^3}$ 2.5); 7.60 br.d.d (H^5, $^3J_{H^6CCH^5}$ 9.0, $^4J_{H^5CCCH^3}$ 2.5); 7.09 d (H^6, $^3J_{H^6CCH^5}$ 9.0). ^{19}F NMR spectrum ($CDCl_3$): δ_F –73.30 ppm (CF_3). Found, %: C 36.80; H 1.68. $C_{10}H_5ClF_6O_3$. Calculated, %: C 37.21; H 1.55.

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