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Reaction of 2-R-Benzo[*d*]-1,3,2-oxazophosphorin-8-one with Hexafluoroacetone. Synthesis and Steric Structure of 3-Phenyl-9,9-bis(trifluoromethyl)-2-ethoxybenzo[*d*]-1,3,2-oxazaphosphepine-2,8-dione

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Abstract–Reaction of hexafluoroacetone with 2-R-benzo[*d*]-1,3,2-oxazophosphorin-8-ones leads to the formation of seven-membered nitrogen-containing heterocycles, the derivatives of 3-phenyl-9,9-bis (trifluoromethyl)benzo[*d*]-1,3,2-oxaza-phosphepine-2,8-diones. Steric structure of 2,3-diphenyl-9,9-bis (trifluoromethyl)-benzo[*d*]-1,3,2-oxazaphosphepine-2,8-di-one was established by X-ray structural analysis. By hydrolysis of the phosphepines a functionally substituted fluorinated ketone, 2-hydroxy-1-(2′-phenylamino)phenyl-2-trifluoromethyl-3,3,3-trifluoro)propan-1-one, was obtained.

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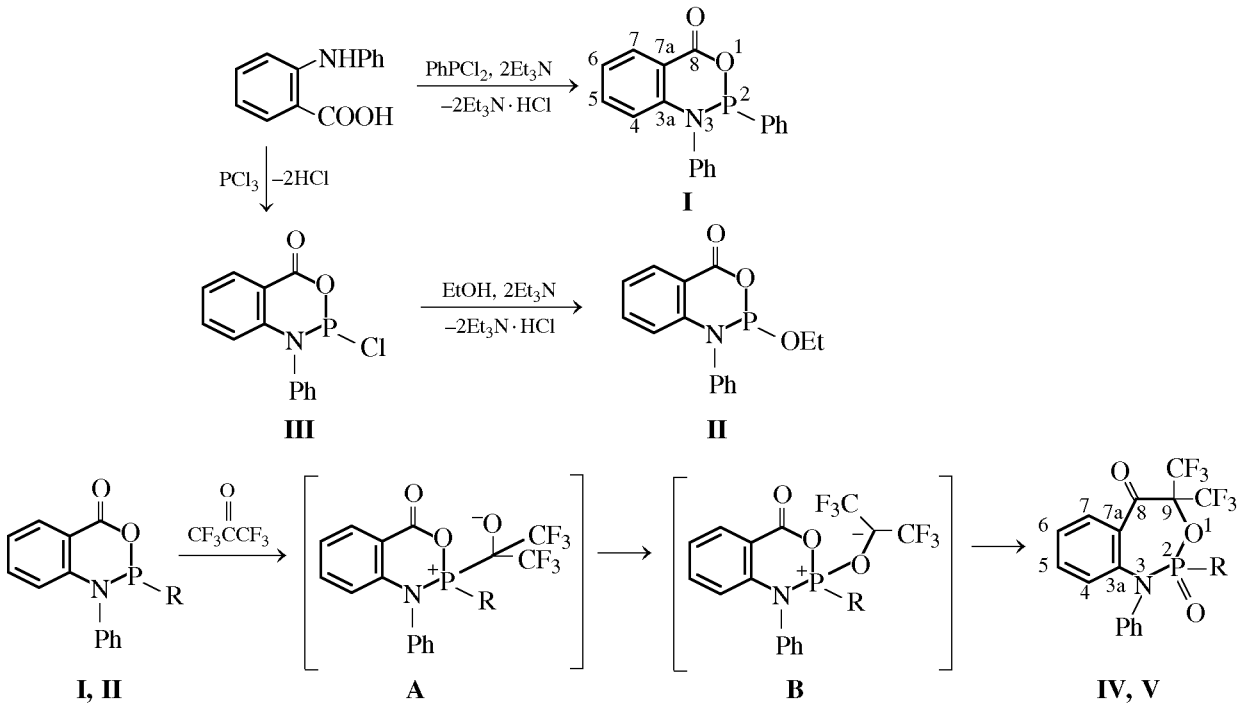
The attention paid to the synthesis and study of chemical properties of P(III)-phosphorylated derivatives of hydroxycarboxylic acids originates from the fact that these compounds are prepared from biologically active precursors like salicylic, mandelic and other acids and therefore they are potentially capable of possessing various biological activity. Another circumstance that attracts attention is their unusual reactivity due to the presence of very reactive P(III)–O–C(O) fragment that is easily attacked by both nucleophiles and electrophiles. When the latter is a compound with activated multiple bond (ketone, aldehyde, imine, etc.), the reaction product is a six- or seven-membered functionally substituted heterocycle (dioxaphosphorinane, dioxaphosphepine, etc.), a P-analog of many biologically active compounds [1–6]. In extention of investigations in this area, in the present work we first obtained P(III)-derivatives underlain by phenylanthranilic acid, 1,3,2-oxazophosphorin-8-ones (**I, II**), with the ring nitrogen atom bound to phosphorus, and studied their reaction with hexafluoroacetone. Synthesis of phosphorines **I** and **II** was carried out along the known procedures (either by reaction of phenylanthranylic acid with phenyldichlorophosphine or by reaction of 3-phenyl-2-chlorobenzo[*d*]-1,3,2-oxazophosphorin-8-one (**III**) with ethanol) [1, 3, 7]. In the ^{31}P-{^{1}H} NMR spectrum to these compounds correspond typical low-field signals at δ_P 121.4 (**I**) and 119.9 (**II**) ppm.

Reaction of compounds **I** and **II** with hexafluoroacetone was carried out under mild conditions (CCl_4, –50°C); it resulted in formation with a high regioselectivity of 2-R-3-phenyl-9,9-bis(trifluoromethyl)-benzo[*d*]-1,3,2-oxa-zaphosphepine-2,8-diones **IV** and **V** respectively. Obviously the reaction of phosphorines **I** and **II** with hexafluoroacetone begins as a nucleophilic attack of phosphorus atom on the carbon atom of the carbonyl group to afford a bipolar ion **A** which further undergoes rearrangement into ion **B**. Further stabilization of ion **B** includes intramolecular nucleophilic substitution at sp^2-hybridized carbon atom resulting in the formation of 1,3,2-oxazaphosphepine **IV** or **V**.

In the ^{31}P–{^{1}H} NMR spectra (CH_2Cl_2) appear signals at δ_P 12.9 (**IV**) and δ_P –6.3 ppm (**V**). In the IR



spectra characteristic adsorption bands are present (ν, cm^{-1}): 1712-1724 (C=O), 1594–1596 (CH_{arom}), 1377 (CF), 1277–1284 (P=O), 1032–1096 cm^{-1} (POC). In the ^{19}F NMR spectra the CF_3 groups give rise to signals in the region of δ_F –69.42 to –76.90 ppm as two quadruplets with the constant $^4J_{FF}$ 9.2–9.8 Hz. In the $^{13}C–\{^1H\}$ NMR spectra of phosphepines **IV** and **V** the following signals are observed that confirm presence of a cyclic fragment: $N^3C^{3a}C^{7a}C^8(O)C^9O^1P^2$: C^8 (δ_C 190.3–191.9), C^{3a} (δ_C 140.7–142.7, $^2J_{PNC}$ 4.1-5.0), C^{7a} (δ_C 133.0–134.9), C^9 (δ_C 82.5–83.1 ppm, $^3J_{FCC}$ 29.8, $^2J_{POC}$ 6.3–10.0 Hz). In the downfield region (140.8–141.5 ppm) in the spectra of compounds **IV** and **V** appears a doublet corresponding to sp^2-hybridized carbon atom C^{10} ($^2J_{PNC}$ 4.4–5.5 Hz). The signals of $C^{11–15}$ nuclei in phenyl substituent at the N atom appear in the region of δ_C 126.1–129.6 ppm. The chemical shifts of $C^{4–7}$ nuclei are interpreted taking into account a small difference in *ortho*- and *para*-effects of shielding by N^3 atom and deshielding by C=O substituent and in keeping with the signal multiplicity. The signals of carbon atoms in trifluoromethyl groups appear at 119.72–120.10 ppm as typical quadruplets of doublets with the constants $^1J_{FF}$ 289.1–289.7 and $^3J_{POCC}$ 5.8–14.8 Hz. In the $^{13}C–\{^1H\}$ NMR spectrum of compound **IV** the atoms $C^{16}–^{21}$ in the phenyl substituent at the phosphorus atom resonate at 128.3–133.3 ppm as doublets with typical spin–spin coupling constants with phosphorus nucleus, $^1J_{PC}$ 185.2, $^3J_{PCCC}$ 16.0, $^2J_{PCC}$ 9.9–10.0, $^4J_{PCCCC}$ 2.8 Hz. The signals of compound **IV** are interpreted on the basis of ATP experiments. Figure 1 shows fragments of $^{13}C–\{^1H\}$ NMR spectra and ATP.

The structure of phosphepine **IV** was also confirmed by X-ray structural analysis. Fig 2 shows geometry of compound **IV**; Table 1 contains selected geometric parameters of the molecule. The conformation of oxazaphosphepine heterocycle is a strongly distorted *boat* with planar fragment of four atoms, $N^3C^{3a}C^{7a}C^8$, the residual atoms (P^2, O^1, C^9) are deviated from the plane to the same side by different distances, –1.396(1), –1.837(2), and –1.053(3) Å respectively. The carbonyl group C^8=O^8 is considerably displaced from the plane of *ortho*-phenylene fragment [torsion angle $O^8C^8C^{7a}C^7$ equals –41.9(4)°]. The nitrogen atom has planar-trigonal configuration, its lone electron pair is practically orthogonal to the plane of the *ortho*-phenylene fragment and has conformation more favorable for conjugation with phenyl substituent at N^3 atom [the torsion angle $P^2N^3C^{16}C^{17}$ is –139.6(3)°].

In the phosphepine **IV** crystal the intermolecular interactions of C–H···O type lead to formation of centrosymmetrical H-dimers. The parameters of $C^{15}–H^{15\cdots}O^{2'}$ interactions (1/2 – *x*, 1/2 – *y*, 1 – *z*) are as follows: $H^{15\cdots}O^{2'}$ 2.47 Å, $C^{15\cdots}O^{2'}$ 3.362(5) Å, φ(C^{15}–

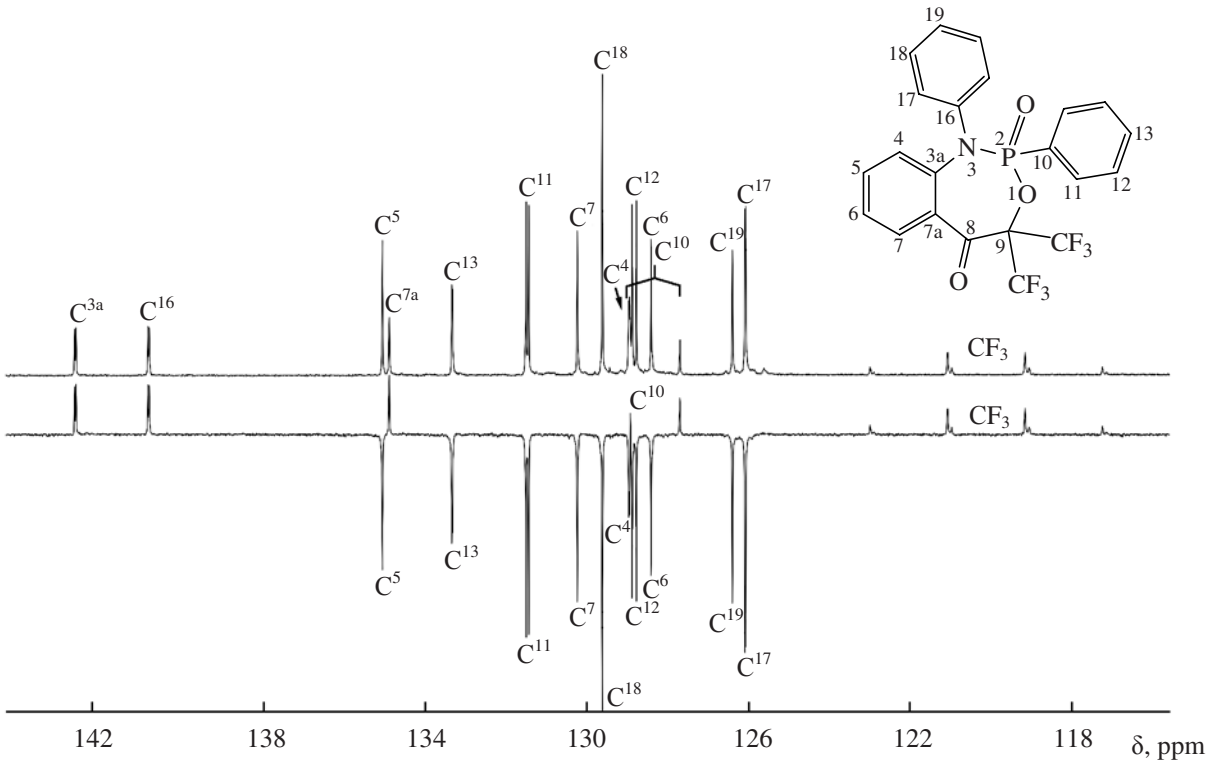


Fig. 1. Fragments of $^{13}C-\{^1H\}$ and ATP (150.6 MHz, $CDCl_3$) NMR spectra of azaphosphepine **IV**.

$H^{15\cdots}O^{2'}$) 160°. Owing to C–H···F interactions such dimers are bound to form an infinite layer parallel to the crystallographic plane (101) (Fig. 3) with hydrophobic aromatic fragments located predominantly on the outer sides of such layers. The

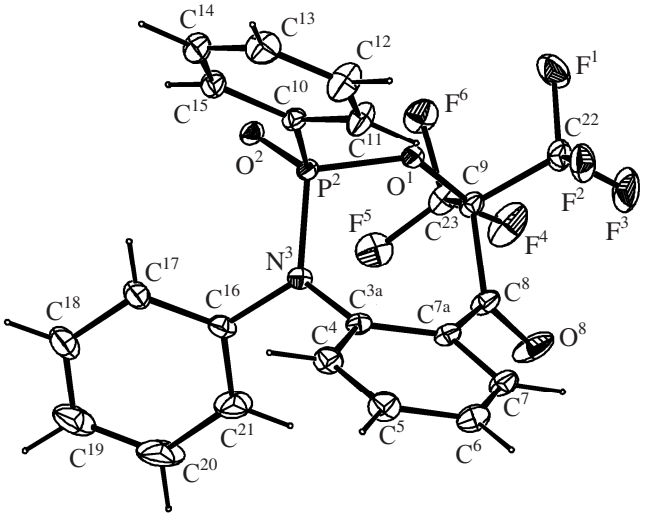


Fig. 2. Geometry of 2,8-dioxo-2,3-diphenyl-9,9-bis (triflu-oromethyl)benzo[*d*]-1,3,2-oxazaphosphepine **IV** in a crystal.

parameters of interaction $C^{18}–H^{18\cdots}F^{5'}$ (1/2 + *x*, –1/2 – *y*, 1/2 + *z*) are as follows: $H^{18\cdots}F^{5'}$ 2.51 Å, $C^{85\cdots}F^{5'}$ 3.441(7) Å, φ($C^{18}–H^{18\cdots}F^{5'}$) 175°.

Analysis of intermolecular interactions showed a significant number of intra- and intermolecular short contacts of F–F type with fluorine–fluorine distances in the range 2.84 to 3.09 Å. If we take the sum of van der Waals radii plus 0.2 Å (to account for temperature factor and errors at the determination of coordinates) as a criterion of contact, then this system of contacts leads to mutual binding of the fluorine-containing fragments of the molecules and formation of three-dimensional lattice (Fig. 4).

Hydrolysis of 1,3,2-oxazaphosphepines **IV** and **V** with ethanol–water (1 : 1) mixture leads to functionally substituted fluorinated ketone, 2-hydroxy-1-(2′-phenylamino)phenyl-2-trifluoromethyl-3,3,3-trifluoropropan-1-one (**VI**). In its ^1H NMR spectrum (DMSO-d_6) the amide and hydroxy group protons resonate in the downfield region as singlets [δ_H 9.15 ppm (NH), 9.94 ppm (OH)]. The trifluoromethyl groups in ^{19}F NMR spectrum appear as singlet in the typical region δ_F –74.51 ppm.

Selected bond lengths (*d*, Å), bond (φ, deg) and torsion (τ, deg) angles

Bond	*d*	Bond	*d*	Bond	*d*
C^{7a}–C^{3a}	1.389 (6)	C^{8}–C^{9}	1.561 (6)	C^{16}–N^{3}	1.449 (5)
C^{7a}–C^{8}	1.473 (6)	C^{9}–O^{1}	1.406 (4)	N^{3}–P^{2}	1.652 (3)
C^{3a}–N^{3}	1.424 (4)	C^{9}–C^{22}	1.548 (6)	O^{1}–P^{2}	1.608 (3)
C^{8}–O^{8}	1.206 (5)	C^{10}–P^{2}	1.780 (4)	O^{2}–P^{2}	1.451 (3)
Angle	φ	Angle	φ	Angle	φ
$O^{8}C^{8}C^{7a}$	122.7 (4)	$O^{1}C^{9}C^{8}$	113.7 (3)	$O^{2}P^{2}O^{1}$	115.8 (2)
$O^{8}C^{8}C^{9}$	116.9 (4)	$C^{10}C^{15}C^{14}$	121.9 (5)	$O^{2}P^{2}N^{3}$	113.6 (2)
$C^{7a}C^{8}C^{9}$	120.1 (3)	$C^{7b}N^{3}C^{16}$	116.8 (3)	$O^{1}P^{2}N^{3}$	101.5 (2)
$O^{1}C^{9}C^{22}$	111.4 (3)	$C^{7b}N^{3}P^{2}$	119.2 (2)	$O^{2}P^{2}C^{10}$	114.5 (2)
$O^{1}C^{9}C^{23}$	101.7 (4)	$C^{16}N^{3}P^{2}$	122.1 (3)	$O^{1}P^{2}C^{10}$	99.8 (2)
$C^{22}C^{9}C^{23}$	111.6 (4)	$C^{9}O^{1}P^{2}$	129.3 (3)	$N^{3}P^{2}C^{10}$	110.1 (2)
Angle	τ	Angle	τ	Angle	τ
$O^{2}P^{2}O^{1}C^{9}$	–78.4	$O^{2}P^{2}N^{3}C^{16}$	–23.92	$P^{2}N^{3}C^{16}C^{17}$	138.6
$N^{3}P^{2}O^{1}C^{9}$	45.2	$O^{1}P^{2}C^{10}C^{11}$	–30.3	$C^{3a}C^{16}C^{21}$	122.3
$C^{10}P^{2}O^{1}C^{9}$	158.2	$O^{2}P^{2}C^{10}C^{11}$	–154.7	$P^{2}N^{3}C^{3a}C^{7a}$	–73.20
$O^{1}P^{2}N^{3}C^{3a}$	47.5	$P^{2}O^{1}C^{9}C^{23}$	177.5	$C^{16}N^{3}C^{3a}C^{4}$	–55.8
$O^{2}P^{2}N^{3}C^{3a}$	172.5	$P^{2}O^{1}C^{9}C^{8}$	–67.2	$C^{7b}C^{7a}C^{8}C^{9}$	52.3
$C^{10}P^{2}N^{3}C^{3a}$	–57.5	$P^{2}O^{1}C^{9}C^{22}$	58.5	$C^{7}C^{7a}C^{8}O^{8}$	41.7
$O^{1}P^{2}N^{3}C^{16}$	–148.9	$P^{2}N^{3}C^{16}C^{21}$	–41.6	$O^{8}C^{8}C^{9}O^{1}$	178.0

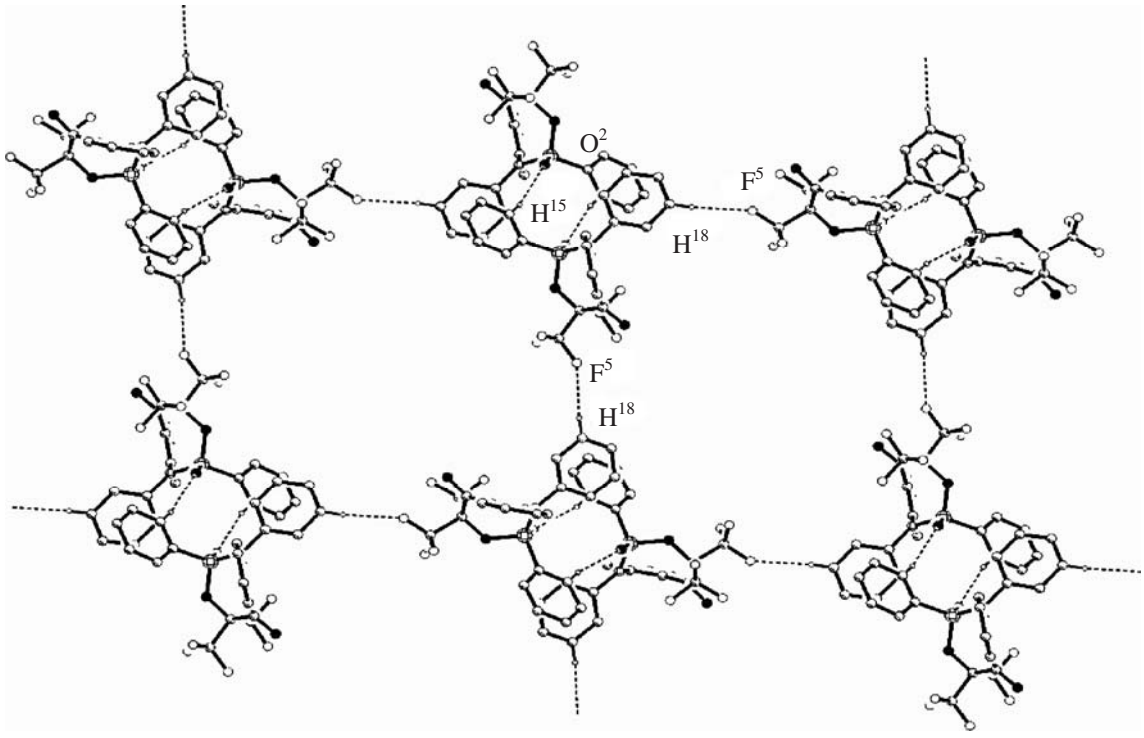


Fig. 3. Intermolecular C–H···O and C–H···F interactions (dot lines) in a crystal of compound **IV** (only the hydrogen atoms involved in the interaction are shown).

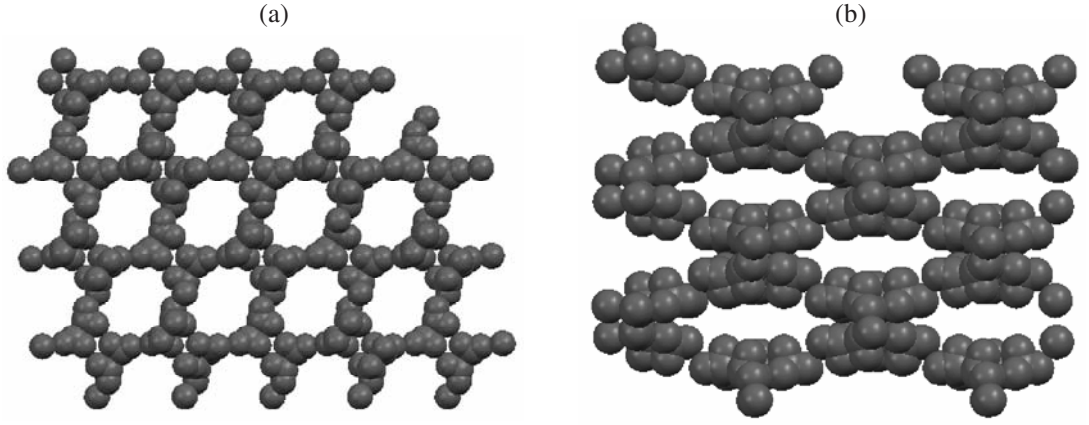
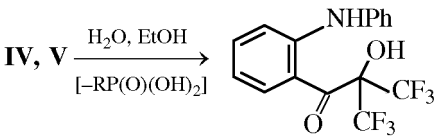


Fig. 4. Two projections on infinite lattice in the crystal of compound **IV**: (a) View along 0*b* axis, (b) View along 0*c* axis. The fluorine-containing fragments are imaged in van der Waals radii, other atoms are not shown.



VI

Thus the reaction of 2-R-3-phenylbenzo[*d*]-1,3,2-oxazophosphorin-8-ones **II** and **III** with hexafluoroacetone manifests specificity of the chemical properties of phosphorus heterocycles, namely, the easy cleavage of the macroergic PO–C(O) bond and the ready formation of a new C–C bond. Like with the 2-R-benzo[*d*]-1,3,2-dioxaphosphorin-4-one derivatives, in this case the betaine **A** is unstable and undergoes P^+–O–C^- rearrangement. In the bipolar ion **B** the nucleophilic substitution at the sp^2-hybridized carbon atom occurs faster than addition of the second hexafluoroacetone molecule at the anionic center. It also should be noted that these reactions are regioselective, leading to the formation of 1,3,2-oxazaphosphepines only; hydrolysis of the latter allows a preparation of fluorinated hydroxyketons hardly accessible by other methods.

EXPERIMENTAL

The IR spectra were recorded on a Specord M-80 instrument from thin films or from suspensions of compounds in mineral oil between KBr plates. The NMR spectra were registered on a spectrometer Varian Unity-300 (^{1}H, 300 MHz; ^{31}P, 121.42 MHz; ^{19}F, 287.2 MHz). The ^{13}C, ^{13}C–{^{1}H} and ATP NMR spectra were obtained on a Bruker Avance-600 instrument (150.9 MHz). Chemical shifts ^{1}H and ^{13}C were measured relatively to the residual protons or carbon nuclei of the solvent. The ^{31}P NMR spectra were measured relatively to the external reference H_3PO_4. The ^{19}F NMR spectra were recorded in $CDCl_3$ with the internal reference C_6F_6, and then chemical shifts were recalculated to $CFCl_3$.

2,3-Diphenylbenzo[*d*]-1,3,2-oxazophosphorin-8-one (I). To a mixture of 0.22 mol of phenylanthranylic acid and 0.44 mol of triethylamine in ether (250 ml) at –30°C was added dropwise with stirring a solution of phenyldichlorophosphine (0.22 mol) in ether (30 ml). The reaction mixture was stirred till it warmed to 20°C. Triethylammonim chloride precipitate was filtered off, and ether was removed by distillation. The residue was dissolved in 15 ml of a mixture of diethyl ether with pentane (1 : 1) and left for crystallization at 0°C. Compound **I** was then isolated as yellow crystals in 84% yield, mp 70–72°C. ^{31}P–{H} NMR spectrum (CH_2Cl_2): δ_P 121.4 ppm. Found, %: C 71.47; H 4.38; P 9.72 $C_{19}H_{14}NO_2P$. Calculated, %: C 71.35; H 4.21; P 9.58.

3-Phenyl-2-ethoxybenzo[*d*]-1,3,2-oxazophosphorin-8-one (II). Along the procedure for the synthesis of salicylphosphites from 0.09 mol of phenylanthranylic acid and 0.12 mol of PCl_3 compound **III** was prepared as a viscous liquid in 88% yield. ^{31}P–{^{1}H} NMR spectrum (CH_2Cl_2): δ_P 135.9 ppm. IR spec-trum, cm^{-1}: 1748, 1596, 1516, 1456, 1276, 1224, 1160, 1120, 1016, 892, 752, 696. To 0.08 mol of compound **III** in 150 ml of ether was added 1 : 1 mixture of ethyl alcohol and triethylamine (0.08 mol each) in 20 ml of ether at –20°C. The triethylammonium chloride precipitate was filtered off, ether was removed by distillation. The residue contained compound **II** as a viscous liquid, yield 87%. ^{31}P–{^{1}H} NMR spectrum

(toluene): d_P 119.9 ppm. IR spectrum, cm^{-1}: 1736, 1604, 1456, 1304, 1158, 1040, 876, 756, 696.

Reactions of compounds I and II with hexafluoroacetone. To a solution of 1,3,2-oxazophosphorine **I** or **II** (0.01 mol) in 30–40 ml of CCl_4 was condensed hexafluoroacetone till the gain in weight corresponding to 0.011 mol. The reaction mixture was allowed to attain room temperature and left for 3 days. The solvent was removed under a vacuum of 3 mm Hg, and benzo[*d*]-1,3,2-oxazaphosphepine **IV** or **V** was obtained in residue as a viscous liquid. 2,3-Diphenyl-9,9-bis(tri-fluoromethyl)benzo[*d*]-1,3,2-oxazaphosphepine-2,8-dione **IV** can be crystallized gradually from ether at 0°C as colorless crystals in 47% yield, mp 153°C. IR spectrum, cm^{-1}: 3067, 2924, 2854, 1712, 1594, 1451, 1277, 1141, 1066, 980, 886, 743, 691, 667, 566. The $^{31}P–\{^1H\}$ NMR spectrum (CCl_4): δ_P 12.9 ppm. ^{19}F NMR spectrum ($CDCl_3$), d_F, ppm, *J,* Hz: –69.42 q (CF_3, $^4J_{FF}$ 9.2), –74.34 q (CF_3, $^4J_{FF}$ 9.2). ^1H NMR spectrum ($CDCl_3$), δ, ppm, *J,* Hz: 7.64 br.m ($H^{17,21}$, $^3J_{PH}$ 13.8, $^3J_{HH}$ 7.6–7.8), 7.60 m (H^7), 7.58 br.d.d. (H^5, $^3J_{HH}$ 7.5, $^3J_{HH}$ 7.5), 7.42–7.44 m ($H^{18,20}$, H^{13}, H^{19}), 7.27 br.d.d ($H^{12,14}$, $^3J_{HH}$ 7.7–8.0, $^3J_{HH}$ 8.0), 7.16 br.d.d. (H^6, $^3J_{HH}$ 7.5, $^3J_{HH}$ 7.5), 7.13 br.d ($H^{11,15}$, $^3J_{HH}$), 6.69 m (H^4). ^{13}C NMR spectrum (hereinafter in parentheses is given the multiplicity of the signal in $^{13}C–\{^1H\}$ NMR spectrum) ($CDCl_3$, δ_C ppm, *J,* Hz): 142.66 m (d) (C^{3a}, $^2J_{PNC^{3a}}$ 5.0), 128.95 d.d.d (d) (C^4, $^1J_{HC^4}$ 161.9, $^3J_{HC^6CC^4}$ 8.3, $^3J_{PNCC^4}$ 2.8), 135.05 d.d (s) (C^5, $^1J_{HC^5}$ 164.0, $^3J_{HC^7CC^5}$ 8.7), 128.40 d.d (s) (C^6, $^1J_{HC^6}$ 164.6, $^3J_{HC^4CC^6}$ 7.6), 130.23 d.d.d (s) (C^7, $^1J_{HC^7}$ 164.6, $^3J_{HC^5CC^7}$ 6.6, $^2J_{HC^6C^7}$ 4.5), 134.88 br.d.d (s) (C^{7a}, $^3J_{HC^6CC^{7a}}$ 5.4, $^3J_{HC^4CC^{7a}}$ 5.4), 191.89 br.d (s) (C^8, $^3J_{HC^7CC^8}$ 3.9–4.0), 82.48 sept.d (sept.d) (C^9, $^2J_{HCC^9}$ 29.8, $^2J_{POC^9}$ 10), 140.84 m (d) (C^{10}, $^2J_{PNC^{16}}$ 4.4), 126.07 br.d (d) ($C^{11,15}$, $^1J_{HC}$ 161.6, $^3J_{PNCC}$ 2.8), 129.62 d.d (s) ($C^{12,14}$, $^1J_{HC}$ 160.7, $^3J_{HC^{12,14}CC}$ 8.0), 126.39 d.t (s) (C^{13}, $^1J_{HC}$ 163.1, $^4J_{HC^{18,20}CCC^{19}}$ 7.5), 128.30 d.t (d) (C^{16}, $^1J_{PC}$ 185.2, $^3J_{HCCC}$ 7.9–8.0), 131.47 br.d.d.d.d (d) ($C^{17,21}$, $^1J_{HC}$ 162.8, $^2J_{PCC}$ 9.9–10.0, $^3J_{HC^{17}CC^{21}}$ 7.5–7.6, $^3J_{HC^{17,21}CC^{19}}$ 7.5–7.6), 128.82 d.d.d (d) ($C^{18,20}$, $^1J_{HC}$ 163.4, $^3J_{PCCC}$ 16.0, $^3J_{HC^{18,20}CC}$ 8.1), 133.33 d. m (d) (C^{19}, $^1J_{HC^{13}}$ 160.7, $^3J_{HC^{12,14}CC^{13}}$ 7.0–7.4, $^4J_{PCCCC^{13}}$ 2.8), 120.10 q (q) (CF_3, $^1J_{FC}$ 289.1), 120.06 q.d (q.d), (CF_3, $^1J_{FC}$ 289.7, $^3J_{POCC}$ 14.8). 3-Phenyl-9,9-bis-(trifluoromethyl)-2-ethoxy-benzo[*d*]-1,3,2-azaphosphepin-2,8-dione (**V**), viscous liquid, yield 52%. IR spectrum, ν, cm^{-1}: 1724, 1598, 1492, 1452, 1284, 1140, 1032, 980, 888, 768, 700, 672. $^{31}P–\{^1H\}$ NMR spectrum (CCl_4): δ_P –6.3 ppm. ^{19}F NMR spectrum ($CDCl_3$, δ_F ppm, *J,* Hz): –74.34 q (CF_3, $^4J_{FF}$ 9.2), –76.90 q (CF_3, $^4J_{FF}$ 9.8). ^1H NMR spectrum (300 MHz, $CDCl_3$, δ ppm, *J,* Hz): 1.24 t.d (CH_3, $^3J_{POCH}$ 1.0, $^3J_{HH}$ 7.1), 4.25 m (OCH_2); the protons of phenyl rings resonate as a multiplet at δ 6.94–7.52 ppm. ^{13}C NMR spectrum ($CDCl_3$, δ_C ppm, *J,* Hz): 140.67 d (m) (C^{3a}, $^2J_{PNC^{3a}}$ 4.1), 127.12 d (d.m) (C^4, $^1J_{HC^4}$ 170.0, $^3J_{PNC^{3a}C}$ 3.6), 134.95 s (d.d) (C^5, $^1J_{HC^5}$ 164.2, $^2J_{HC^4C}$ 8.7), 127.32 s (d.d) (C^6, $^1J_{HC^6}$ 164.2, $^2J_{HCC}$ 7.3), 130.31 s (d.m) (C^7, $^1J_{HC^7}$ 163.8), 133.04 s (m) (C^{7a}), 190.29 s (d) (C^8, $^3J_{HC^7CC}$ 3.3), 83.11 sept.d (sept.d) (C^9, $^2J_{FCC}$ 29.8, $^2J_{POC^9}$ 6.3), 141.50 d (m) (C^{10}, $^2J_{PNC^{14}}$ 5.5), 126.30 d (d.m) ($C^{11,15}$, $^1J_{HC}$ 160.8, $^3J_{PNCC}$ 3.1), 129.51 s (d.d) ($C^{12,14}$, $^1J_{HC}$ 162.3, $^2J_{HC^{17}C}$ 8.3), 126.70 s (d.t) (C^{13}, $^1J_{HC^{17}}$ 161.9, $^2J_{HCC}$ 7.3), 65.69 d (t.d.q) (C^{16}, $^1J_{HC^{12}}$ 149.6, $^2J_{POC^{12}}$ 6.3, $^2J_{HC^{13}C}$ 4.4), 15.52 d (q.d.t) (C^{17}, $^1J_{HC^{13}}$ 127.8, $^3J_{POC^{12}C^{13}}$ 7.3, $^2J_{HC^{12}C^{13}}$ 2.9), 119.72 br.q.m (CF_3, $^1J_{FC}$ 289.2, $^1J_{PC}$ 5.8). Found, %: s 49.43; H 3.20; P 7.09. $C_{18}H_{14}F_6NO_3P$. Calculated, %: s 49.39; H 3.16; P 7.05.

Hydrolysis of compounds **IV** and **V** was carried out in 30 ml of 1:1 acidified water–ethanol mixture at 90º for 36 h. Then the reaction mixture was allowed to attain room temperature, extracted with ether, the extract was dried over $MgSO_4$, and evaporated in a vacuum of 12 mm Hg. The residue was 2-hydroxy-1-(2'-phenylamino)phenyl-2-trifluoromethyl-3', 3', 3'-trifluoropropan-1-one (**V**), a slightly yellowish oil. ^1H NMR spectrum (DMSO-d_6, δ, ppm): 9.94 s (NH), 9.15 br.s (OH), 6.7–8.6 m (phenyl group protons). Found, %: C 52.90; H 3.03. $C_{16}H_{11}NO_2F_6$. Calculated, %: C 52.58; H 2.75.

X-Ray structural analysis of compound **IV** was carried out at the Division of Structural Investigations of the Center of Joint Use of Scientific Instruments based on the Laboratory of Diffraction Methods of the Arbuzov Institute (IOPhKh) at Kazan Scientific Center of the Russian Academy of Sciences. The experiment was performed at 20°C on an automatic diffractometer Enraf-Nonius CAD-4 with monochromated CuK_α irradiation (λ 1.54184Å, ω-scan, θ < 74.19°). The crystals of $C_{22}H_{14}F_6NO_3P$ are monoclinic, space group *C*2/*c*, the cell parameters at 20°C are as follows: *a* 26.125(2) Å, *b* 11.402(2) Å, *c* 19.603(3) Å, b 131.087(4)°, *V* 4401(1) $Å^3$, *Z* 8, *M* 485.31, $d_{calc.}$ 1.465 g/cm^3, F(000) 1968. Intensities of 4527 reflexions were measured, of them 3479 had $I > 2s$. No decrease in the intensity of three control reflexions was observed during the experiment. Extinction [μ(Cu) 18.07 cm^{-1}] was taken into account. The structure was solved by the direct method using SIR program [8] and refined initially in isotropic and then in anisotropic approximation using

SHELXL [9] and WinGX [10] programs. Coordinates of hydrogen atoms were calculated on the basis of stereochemical criteria and refined along the "rider" model. The final values of divergence factors were R 0.0452, R_W 0.1202 for 3479 independent reflexions with $F^2 \geq 4(F_0)$. Preliminary the data obtained were treated with MolEN [11] program. Analysis of molecular and crystal structures and intermolecular interactions was carried out with PLATON [12] program. Atomic coordinates and their thermal parameters for compound **IV** are deposited in the Cambridge Data-base of X-ray Structural Data, No. CCDC 651586.

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