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To the 80th Anniversary of B.I. Ionin

Caged C–P Phosphoranes Based on 2-(2-Methyl-4-oxopent-2-yloxy)- and 2-[2-(Methylcarbonyl)-1-phenoxy]-1,3,2-benzodioxaphospholes and Diethyl Mesoxalate

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Abstract—Cascade reactions of 2-(2-methyl-4-oxopent-2-yloxy)- and 2-[2-(methylcarbonyl)-1-phenoxy]-1,3,2-benzodioxaphospholes with diethyl mesoxalate yield caged phosphoranes containing a phosphorus–carbon bond: 7,7-bis(ethoxycarbonyl)-3,3,5-trimethyl-1,1-phenylenedioxy- and 7,7-bis(ethoxycarbonyl)-5-methyl-1,1-phenylenedioxy-3,4-benzo-2,6,8,1λ^5-trioxaphosphabicyclo[3.2.1$^{1.5}$]octanes. Spatial structure of latter product has been determined by X-ray diffraction analysis.

Keywords: diethyl ketomalonate, benzodioxaphosphole, caged phosphorane, cascade reaction

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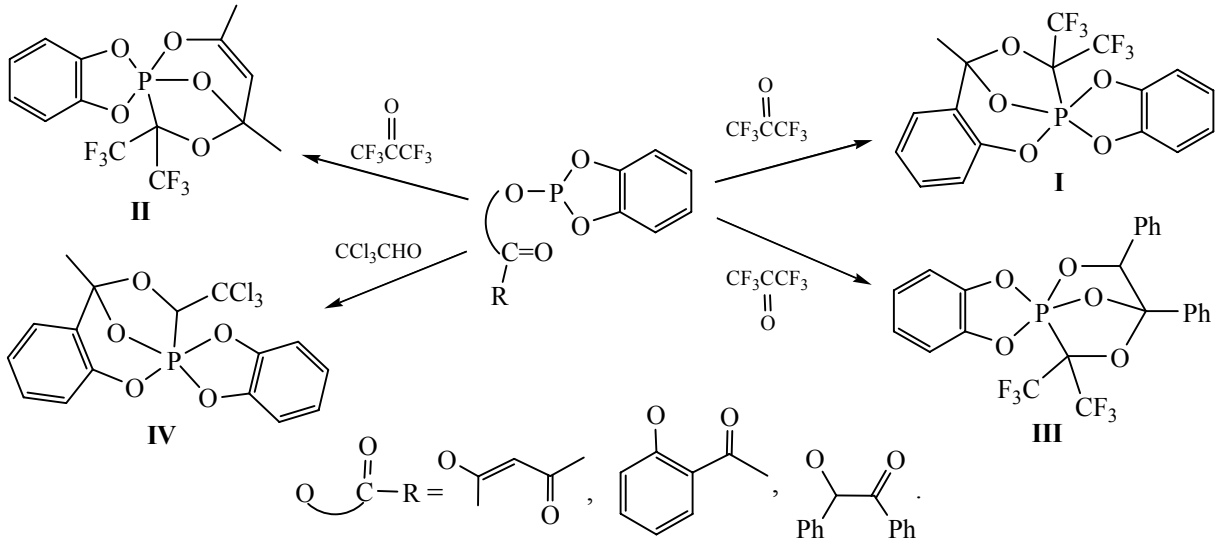
Five-coordinate phosphorus derivatives are key intermediates in (de)phosphorylation biochemical reactions (crucial for cell energetics, DNA or RNA information recording, and other processes [1, 2]) as well as in organic synthesis (Wittig reaction [3, 4], Mitsunobu reaction [5–8], Evans reaction [9], oxaphosphorane condensation [10–12], etc). Phosphoranes are most commonly synthesized via oxidative addition of P(III) derivatives (see reviews in [13, 14]). We have recently shown that five-coordinate phosphorus compounds can be prepared via cascade reactions of P(III) compounds containing an endo- or exocyclic carbonyl group in γ or δ position with respect to phosphorus; the process is promoted by active carbonyl compounds such as chloral or hexafluroacetone [15–20]. Scheme 1 presents the formation of caged phosphoranes **I**–**IV** from phospholes containing an exocyclic carbonyl group [15–18].

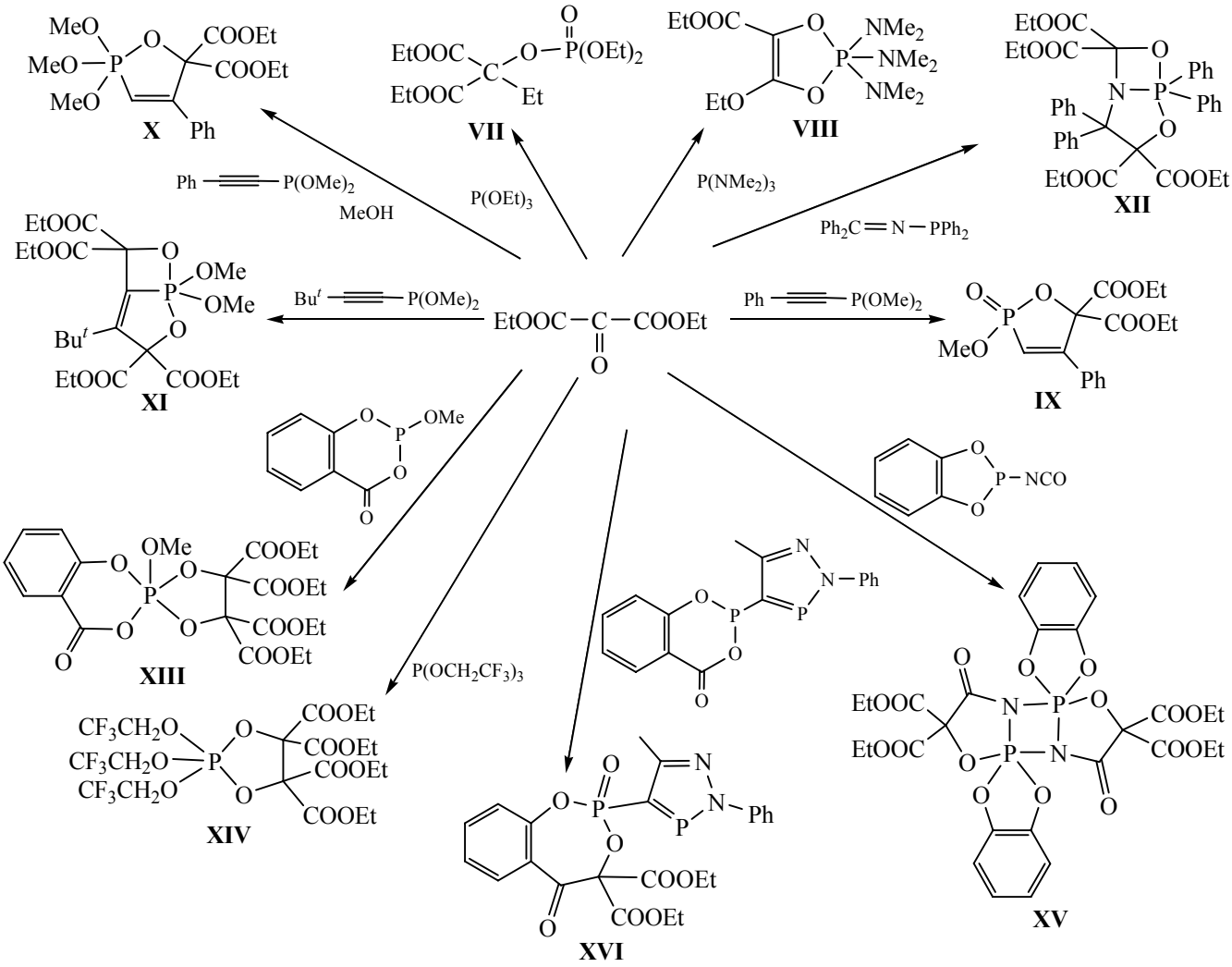
In the present work we extended the above-described approach to diethyl mesoxalate (diethyl ketomalonate) and 2-(2-methyl-4-oxopent-2-yloxy)- and 2-[2-(methylcarbonyl)-1-phenoxy]-1,3,2-benzodioxaphospholes (**V** and **VI**) containing an exocyclic carbonyl group in the δ-position.

Diethyl mesoxalate reacts with P(III) compounds to give P(IV) and P(V) derivatives of various composition. Scheme 2 summarizes pathways diversity of diethyl mesoxalate reactions with different P(III) derivatives: triethyl phosphite yields phosphate **VII** [21], hexamethylphosphoramidite yields phosphorane **VIII** 1 : 1 [22], dimethyl (phenylethynyl)phosphonite yields oxaphospholenes with a four- and a five-coordinate phosphorus atom **IX** and **X** [23], dimethyl-(*tert*-butylethynyl)phosphonite and *N*-(diphenylphosphanyl)-1,1-diphenylmethanimine yield unusual bicyclic phosphoranes **XI** and **XII** [24, 25], 2-methoxy-4*H*-1,3,2-benzodioxaphosphinin-4-one and tris(2,2,2-trifluoroethyl) phosphite yield phosphoranes with **XIII** and **XIV** containing dioxaphospholane [26], 2-isocyanato-1,3,2-benzodioxaphosphole yields diazadi-

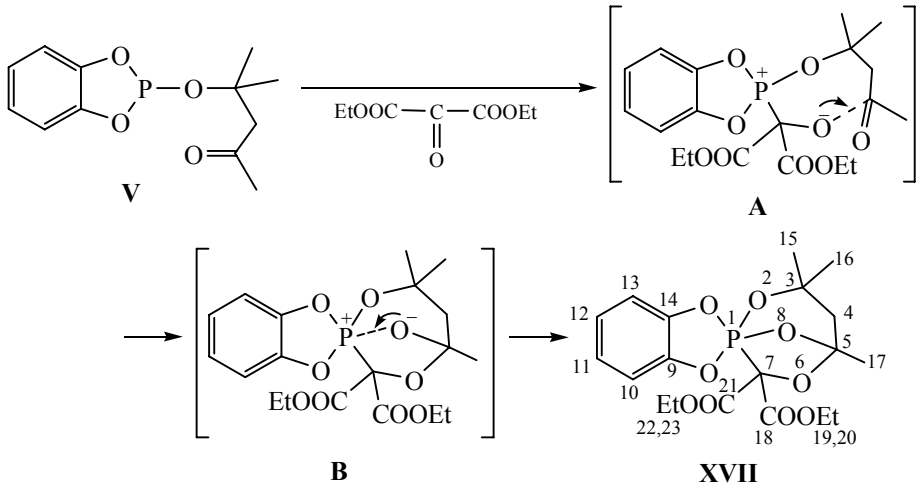
Scheme 1.



Scheme 2.



Scheme 3.



phosphetidine derivative **XV** [27], and 2-(5-methyl-2-phenyl-2*H*-1,2,3-diazaphosphol-4-yl)-4*H*-benzo[*d*]-[1,3,2]dioxaphosphinin-4-one undergoes extension of the six-membered ring to form a seven-membered ring phosphepine **XVI** [28].

Reaction of phosphole **V** with diethyl mesoxalate (Scheme 3) under mild conditions in inert atmosphere at the 1 : 1 reagent ratio (the latter was in contrast to most of the above-mentioned examples) gave a caged phosphorane **XVII**; $^{31}P–\{^1H\}$ NMR spectrum (CH_2Cl_2) of the product contained a singlet signal at δ_P –25.7 ppm. After the reaction mixture was treated with pentane, compound **II** was formed as crystals highly sensitive to hydrolysis.

The reaction seemingly started with attack of the phosphorus atom of phosphite **V** at the carbonyl carbon atoms of the highly reactive diethyl mesoxalate to form a bipolar ion **A,** the latter being further transformed into a bipolar ion **B** via intramolecular attack of the alkoxide ion at the acetyl carbon atom. Apparently, that reaction route was kinetically controlled, occurring much faster that alternative rearrangement $P^+–C–O^- \rightarrow P^+–O–C^-$ or reaction with the second molecule of diethyl mesoxalate (cf. the case of unsubstituted trialkyl phosphites). The following attack of the alkoxide anion at phosphorus in betaine **B** gave the final reaction product: caged phosphorane **XVII**.

Even though the reaction product contained two chiral centers (P and C^5), it was formed as a single diastereomer. Its structure was confirmed by ^1H and ^{13}C NMR spectroscopy and electron-impact mass spectrometry. The mass spectrum contained a molecular ion peak at *m*/*z* 428, corresponding to structure **XVII**. The IR spectrum contained no bands assignable to carbonyl group of the starting phosphole **I** but showed ester bands at 1754 and 1741 cm^{-1}. The $^{13}C–\{^1H\}$ and ^{13}C NMR spectra contained a characteristic upfield doublet (δ_C 79.99 ppm) assigned to the $P–C^7$ fragment ($^1J_{PC7}$ 155.2 Hz). The remarkable broadening of signals of the $C^9–C^{14}$ carbon atoms and the corresponding protons $_{H10}–H^{13}$ was likely due to pseudorotation of the phosphorus trigonal bipyramid in the benzodioxaphosphole ring. The ^1H and ^{13}C NMR spectra evidenced about nonequivalence of the ethoxycarbonyl groups due to their fixed arrangement in the bicyclic scaffold. Moreover, the ^1H NMR data pointed at nonequivalence of protons within each of the ethoxycarbonyl groups: those protons appeared as AB parts of ABX_3-type spectra. Figure 1 shows ^1H NMR spectra of the H^{19} and H^{22} protons and the simulated spectra for the corresponding systems (MestRe-C [29]).

The reaction of diethyl mesoxalate with phosphole **VI** with exocyclic carbonyl group linked to phosphorus by a more rigid (oxyphenylene) spacer (Scheme 4) resulted in nearly quantitative formation of the phosphorane. $^{31}P–\{^1H\}$ spectrum of the product contained a signal at δ_P –24.1 ppm (CH_2Cl_2), and its mass spectrum showed a molecular ion peak at *m*/*z* 448, pointing at the 1 : 1 composition. The presence of more rigid exocyclic substituent could enhance probability of the $P^+–C–O^- \rightarrow P^+–O–C^-$ rearrangement, but it was not observed. The $^{13}C–\{^1H\}$ NMR spectrum unambiguously evidenced about structure **XVIII** with

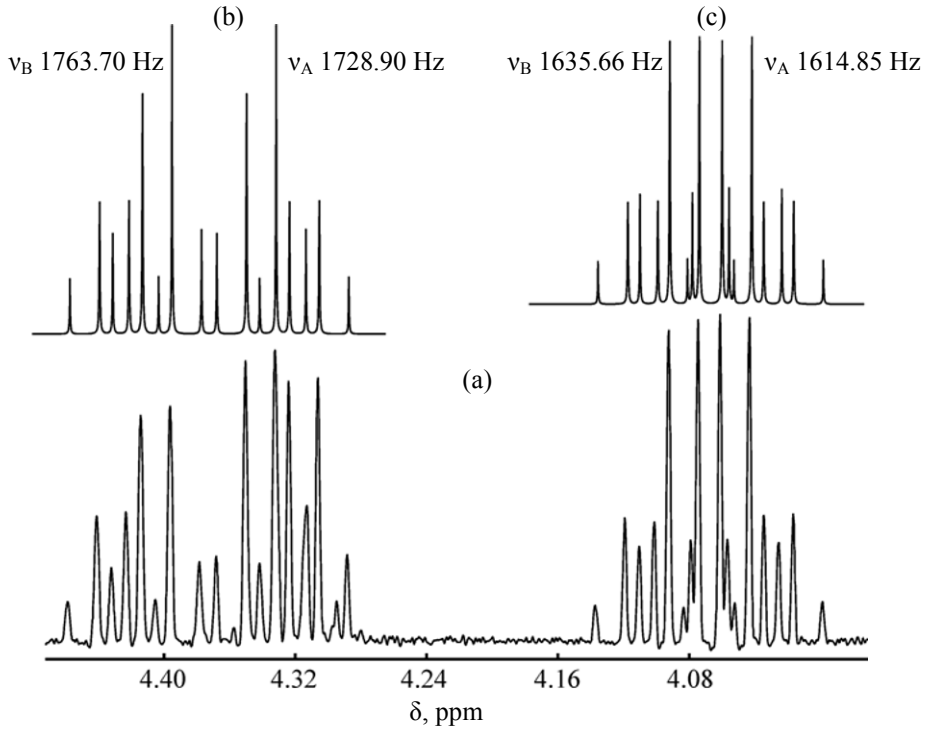


Fig. 1. Fragment of the ^{1}H NMR spectrum (400 MHz, $CDCl_3$) (a) of compound **XVII** (the $COOCH_2$ proton resonance signal is shown) and simulated spectra (b) $^2J(H_AH_B)$ 10.63, $^3J(H_AH_X)$ 7.33, $^3J(H_BH_X)$ 7.33 Hz, and (c) $^2J(H_AH_B)$ 10.30, $^3J(H_AH_X)$ 7.34, $^3J(H_BH_X)$ 7.34 Hz.

a phosphorus–carbon bond (δ_C 82.80 ppm, $^1J_{PC7}$ 155.2 Hz). Broadening of the C^9–C^{14} and H^{10}–H^{13} signals, similarly to the case of compound **XVII**, was consistent with pseudorotation in the phosphorus trigonal bipyramid. Presumably, that process removed the nonequivalence of the two possible diastereomers (P and C^7 being the chiral centers); therefore, no conclusion about stereoselectivity of the reaction was possible. In the ^{1}H NMR spectrum ($CDCl_3$), the H^{15}–H^{18} aromatic protons resonated at 7.11–6.92 ppm, the methylene groups of the nonequivalent ethoxycarbonyl substituents appeared as ABX_3 multiplets, and the $C^{19}H_3$ protons gave an upfield doublet ($^4J_{PH}$ 1.9 Hz). Thus, in that case, the intramolecular attack of the P^+–C–O^- alkoxide oxygen on the exocyclic carbonyl group was preferred over other possible reaction routes as well.

The structure of phosphorane **XVIII** was additionally confirmed by X-ray diffraction analysis (Fig. 2 and table). Configuration of the chiral atoms was $C^5_SP^1_S/C^5_RP^1_R$. Phosphorus polyhedron was a trigonal pyramid with planar [within 0.0253(4) Å] base containing P^1, O^2, O^3, and C^7 atoms. The apical O^8 and O^1 atoms deviated from that plane by 1.622(1) and 1.705(1) Å [the P^1–O^1 and P^1–O^8 bond lengths were of 1.680(2) and 1.664(2) Å, the $O^3P^1O^8$ bond angle was of 172.78(7)°]. The $O^1P^1C^7$, $O^1P^1O^2$, $O^1P^1O^3$, $O^8P^1C^7$, $O^3P^1O^8$, and $O^2P^1O^8$ bond angles were of 85.55(6)°–96.83(7)°, pointing at almost regular trigonal bipyramidal configuration of the phosphorus atom. That was further evidenced by the sum of the $O^2P^1O^3$, $O^3P^1C^7$, and $O^2P^1C^7$ bond angles in the base of the trigonal bipyramid, being equal to 359.98(7)°. The equatorial P^1–O^3 and P^1–O^2 bonds were slightly shorter than the axial ones [1.615(2) and 1.592(2) Å]; the equatorial P^1–C^7 bond length was of 1.877(2) Å. The $P^1O^1C^9C^{14}O^3$ five-membered ring was planar (Fig. 2) within 0.010(1) Å; the O^2, O^8, and C^7 atoms deviated from that plane by 1.442(1), 0.174(1), and 1.342(2) Å, respectively. The benzodioxaphosphinane ring attained the *sofa* conformation with the $P^1O^1C^9C^{14}O^3$ fragment of the heterocycle being planar within 0.031(2) Å and the O^8 atom deviating from the plane by 0.816(1) Å. The C^{19} and O^1 atoms were in equatorial positions [their deviations from the $P^1O^1C^9C^{14}O^3$ plane were of 0.522(3) and –0.864(1) Å, respectively]; the O^3, C^7, and O^6 atoms were in axial positions and deviated from the $P^1O^1C^9C^{14}O^3$ plane by 1.254(1), –1.511(2), and 1.313(1) Å, respectively. Rigidity of the

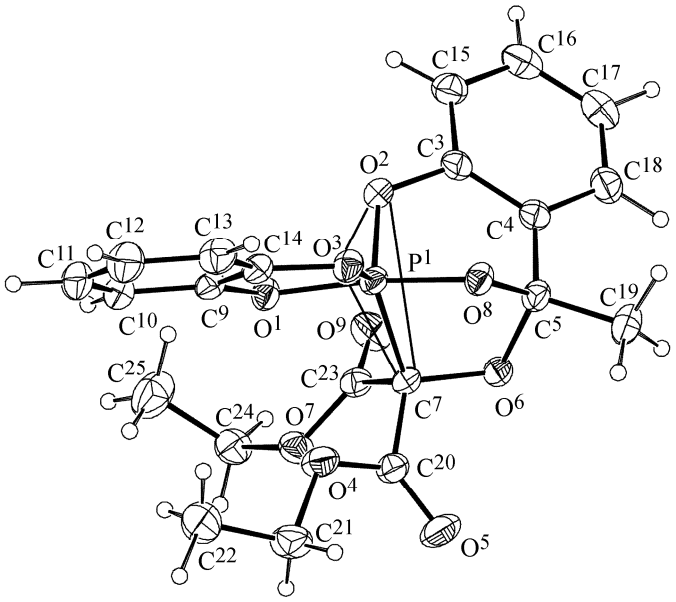


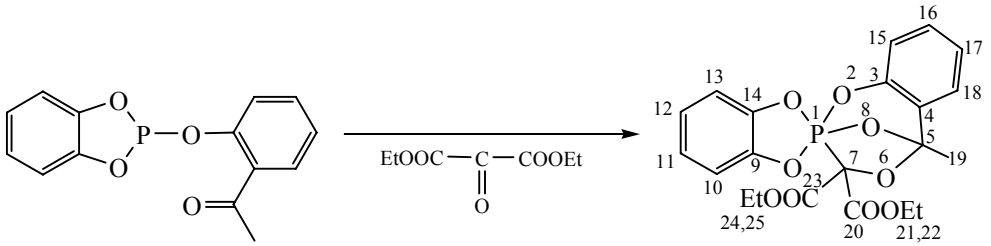
Fig. 2. Molecular geometry of phosphorane **XVIII** in crystal (30% probability thermal ellipsoids are given; the base of the trigonal bipyramid is shown by thin lines).

trioxabicyclooctane scaffold of the molecule was also responsible for the *envelope* conformation of the $P^1C^7O^6C^5O^8$ five-membered ring. At the same time, the $P^1C^7O^6C^5$ fragment was planar within 0.044(1) Å, and the O^8 atom deviated from the $P^1C^7O^6C^5$ plane by 0.657(1) Å. The C^{19}, C^{23}, and O^1 atoms were equatorial [their deviations from the $P^1C^7O^6C^5$ plane being of 0.889(3), –1.174(2), and –0.520(1) Å, respectively], whereas the O^2, O^3, C^4, and C^{20} atoms were axial and deviated from the $P^1C^7O^6C^5$ plane by –1.455(1), 1.086(1), –1.365(2), and 1.361(2) Å, respectively. Noteworthily, the axially located ethoxycarbonyl substituent ($C^7C^{20}O^5O^4C^{21}C^{22}$) could be considered virtually planar [within 0.120(1) Å]. The second, equatorial ethoxycarbonyl substituent contained a shorter planar [within 0.069(2) Å] fragment $C^7C^{23}O^9O^7C^{24}$, and the last ethoxycarbonyl carbon atom C^{25} deviated from the plane by 1.757(4) Å.

Analysis of intermolecular interactions in the crystal of compound **XVIII** performed using PLATON software [30] revealed a short intramolecular contact of the C–H···O type [C^{24}–H^{241}···O^9, parameters: *d*(H···O) 2.30(2) Å, *d*(C···O) 2.709(3) Å, ∠(C–H···O) 104(2)°]. The crystal packing was significantly stabilized by π–π-electron interactions, the majorly between the $C^3C^4C^{15}C^{16}C^{17}C^{18}$ aromatic fragments in the neighboring molecules (parameters: center-to-center interplanar distance *d* 4.189(3) Å, interplanar angle 0°, shortest interplanar distance 3.31 Å) and the $C^9C^{10}C^{11}C^{12}C^{13}C^{14}$ aromatic fragments in neighboring molecules [center-to-center interplanar distance *d* 5.042(4) Å, interplanar angle 1°, shortest interplanar distance 3.30 Å].

To conclude, despite the tendency of diethyl mesoxalate to react with P(III) derivatives to give

Scheme 4.



VI **XVIII**

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

Bond	*d*	Bond	*d*	Bond	*d*
P^1–O^1	1.680(2)	O^3–C^{14}	1.382(2)	O^7–C^{24}	1.460(3)
P^1–O^2	1.592(2)	O^4–C^{20}	1.316(3)	O^8–C^5	1.411(2)
P^1–O^3	1.615(2)	O^4–C^{21}	1.459(3)	O^9–C^{23}	1.188(3)
P^1–O^8	1.664(2)	O^5–C^{20}	1.186(3)	C^3–C^4	1.385(3)
P^1–C^7	1.877(2)	O^6–C^5	1.461(2)	C^4–C^5	1.507(3)
O^1–C^9	1.365(2)	O^6–C^7	1.404(2)	C^7–C^{20}	1.537(3)
O^2–C^3	1.394(2)	O^7–C^{23}	1.320(2)	C^7–C^{23}	1.528(3)
Bond angle	φ	Bond angle	φ	Bond angle	φ
$O^1P^1O^2$	90.38(7)	$O^3P^1O^8$	85.55(6)	$P^1C^7O^6$	106.5(1)
$O^1P^1O^3$	91.54(6)	$O^3P^1C^7$	133.35(8)	$C^5O^6C^7$	111.3(1)
$O^1P^1O^8$	172.78(7)	$O^8P^1C^7$	85.89(7)	$O^2C^3C^4$	121.5(2)
$O^1P^1C^7$	91.35(7)	$P^1O^1C^9$	112.3(1)	$O^4C^{20}O^5$	125.8(2)
$O^2P^1O^3$	116.24(7)	$P^1O^2C^3$	123.1(1)	$O^6C^5O^8$	106.1(1)
$O^2P^1O^8$	96.83(7)	$P^1O^3C^{14}$	113.6(1)	$O^6C^5C^4$	109.8(1)
$O^2P^1C^7$	110.29(8)	$P^1O^8C^5$	109.4(1)	$C^{20}C^7C^{23}$	111.9(1)
Torsion angle	τ	Torsion angle	τ	Torsion angle	τ
$C^7P^1O^1C^9$	134.3(1)	$C^7P^1O^3C^{14}$	–94.8(1)	$O^8P^1C^7O^6$	–28.0(1)
$O^1P^1O^2C^3$	–150.0(1)	$O^2P^1O^8C^5$	–67.4(1)	$O^8P^1C^7C^{20}$	90.3(1)
$O^3P^1O^2C^3$	118.1(1)	$C^7P^1O^8C^5$	42.6(1)	$O^8P^1C^7C^{23}$	–144.9(1)
$O^8P^1O^2C^3$	29.7(1)	$O^1P^1C^7O^6$	158.7(1)	$P^1O^2C^3C^4$	2.6(2)
$C^7P^1O^2C^3$	–58.4(2)	$O^2P^1C^7O^6$	67.8(1)	$P^1O^8C^5O^6$	–46.2(2)
$O^2P^1O^3C^{14}$	89.8(1)	$O^3P^1C^7O^6$	–107.9 (1)	$P^1O^8C^5C^4$	71.3(1)

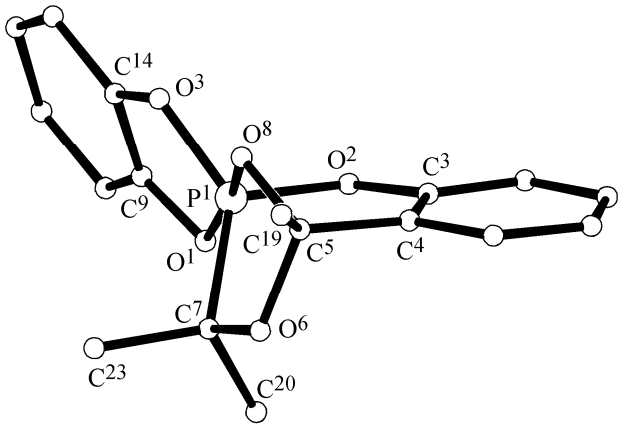


Fig. 3. Conformations of the rings of the trioxaphosphabicyclooctane scaffold of molecule **XVIII** in crystal (for the sake of simplicity, hydrogen atoms are not shown, and only C^{20} and C^{23} are put instead of the ethoxycarbonyl substituents).

1,3,2-dioxaphospholanes containing a five-coordinate phosphorus atom, its reactions with 2-(2-methyl-4-oxopent-2-yloxy)- and 2-[2-(methylcarbonyl)-1-phenoxy]-1,3,2-benzodioxaphospholes followed a kinetically more favorable route involving transfer of the reaction center to the exocyclic carbonyl group of the starting benzophosphole to form caged phosphoranes containing a phosphorus–carbon bond.

EXPERIMENTAL

^1H, ^{13}C, ^{13}C–{^1H}, and ^{31}P–{^1H} NMR spectra of the solutions in $CDCl_3$ were recorded with Bruker-400 and Bruker-600 (^{13}C) spectrometers relative to residual proton signals (^1H) or the ^{13}C resonance of the solvent. IR spectra (KBr pellets) were measured using a Bruker Vector-22 instrument. Mass spectra were obtained with a Thermo Electron DFS instrument (electron

energy 70 eV, ion source temperature 290°C; the direct probe injection with heating from 100 to 350°C; the data were processed using Xcalibur software).

Phospholes **V** and **VI** were synthesized as described elsewhere [17, 18].

7,7-Bis(ethoxycarbonyl)-3,3,5-trimethyl-1,1-phenylenedioxy-2,6,8,1λ^5-trioxaphosphabicyclo-[3.2.1^{1,5}]-octane (XVII). A solution of 1.89 g (0.01 mol) of diethyl mesoxalate in 5 mL of CH_2Cl_2 was added to a cooled (5°C) mixture of 2-(2-methyl-4-oxopent-2-yloxy)-1,3,2-benzodioxaphosphole (**V**) (2.78 g, 0.01 mol); the mixture self-heating was observed. The reaction mixture was incubated during 7 days at 20°C and then diluted with 20 mL of pentane. The crystals that formed in about 10–12 days were filtered off and dried in vacuum (10 mmHg). Yield 4.0 g (95%), mp 97°C. IR spectrum, ν, cm^{-1}: 3465, 3428, 2985, 2957, 2937, 2905, 1759, 1741, 1626, 1601, 1493, 1473, 1451, 1385, 1366, 1347, 1284, 1237, 1218, 1147, 1115, 1070, 1045, 998, 928, 908, 881, 853, 806, 746, 718, 647, 614, 575, 539, 499, 469, 431. ^{1}H NMR spectrum (400 MHz, $CDCl_3$), δ, ppm (*J*, Hz): 7.09 m (H^{10}, $^3J_{H11H10}$ 8.0, $^4J_{H12H10}$ 1.5, $^4J_{PH10}$ 1.2), 6.97 m (H^{12}, $^3J_{H13H12}$ 7.9, $^3J_{H11H12}$ 7.6, $^4J_{H10H12}$ 1.4), 6.89 m (H^{13}, $^3J_{H12H13}$ 7.9–8.0, $^4J_{H11CH13}$ 1.1–1.2), 6.88 m (H^{11}, $^3J_{H10H11}$ 8.0, $^3J_{H12H11}$ 7.6, $^4J_{H13H11}$ 1.2, $^5J_{PH11}$ 1.3), 4.04 m [OCH_A, A part of the ABX_3 system, $^3J(H_AH_B)$ 10.6, $^3J(H_AH_X)$ 7.3], 4.09 m [OCH_B, B part of the ABX_3 system, $^3J(H_AH_B)$ 10.6, $^3J(H_BH_X)$ 7.3], 4.32 m [OCH_A, A part of the ABX_3 system, $^3J(H_AH_B)$ 10.6, $^3J(H_AH_X)$ 7.3], 4.41 m [OCH_B, B part of the ABX_3 system, $^3J(H_AH_B)$ 10.6, $^3J(H_BH_X)$ 7.3], 2.66 d (H^4, B part of the AB system, $^3J(H_AH_B)$ 14.6], 2.20 d [H^4, A part of the AB system, $^3J(H_AH_B)$ 14.6], 1.66 d ($^4J_{PH}$ 1.7), 1.59 s ($H^{15,16,17}$), 1.46 d ($H^{15,16,17}$, $^4J_{PH}$ 3.1), 1.37 t (H^{20}, X_3 part of the ABX_3 system, $^3J_{H19H20}$ 7.1), 0.82 t (H^{22}, X_3 part of the ABX_3 system, $^3J_{H23H22}$ 7.1). ^{13}C NMR spectrum (150.9 MHz, $CDCl_3$), δ_C, ppm (*J*, Hz) (hereafter, the data given in parentheses are for the ^{13}C–{^{1}H} spectra): 81.73 br.d.m (d) (C^3, $^2J_{PC3}$ 8.1), 49.65 br.t.m (br.s) (C^4, $^1J_{HC4}$ 128.4), 101.05 d.m (d) (C^5, $^2J_{PC5}$ 7.7, $^2J_{HC5}$ 2.9), 79.99 d (d) (C^7, $^1J_{PC7}$ 155.2), 144.37 m (d) (C^9, $^2J_{PC9}$ 4.8), 111.12 d.d.d.d (br.d) (C^{10}, $^1J_{HC10}$ 164.0, $^3J_{PC10}$ 18.0, $^3J_{HC12C3}$ 7.7, $^2J_{HC10}$ 4.0), 123.16 d.d (s) (C^{11}, $^1J_{HC11}$ 161.8, $^3J_{HC11}$ 8.1), 120.35 d.d (s) (C^{12}, $^1J_{HC12}$ 161.0, $^3J_{HC12}$ 7.7), 110.42 d.d.d (d) (C^{13}, $^1J_{HC13}$ 164.3, $^3J_{PC}13$ 10.9, $^3J_{HC13}$ 8.9), 141.50 m (d) (C^{14}, $^2J_{PC14}$ 7.0), 31.50 q.d.m (d) (C^{15}, $^1J_{HC15}$ 128.0, $^3J_{PC15}$ 14.6, $^3J_{HC15}$ 4.6–4.8), 28.32 q.d.m (d) (C^{16}, $^1J_{HC16}$ 128.0, $^3J_{PC16}$ 4.0, $^3J_{HC16}$ 4.0–4.5), 30.79 br.q.m (br.s) (C^{17}, $^1J_{HC17}$ 128.4), 167.11 br.s (s) (C^{18}), 62.68 t.q (s) (C^{19}, $^1J_{HC19}$ 148.6, $^2J_{HC19}$ 4.4), 14.05 q.t (s) (C^{20}, $^1J_{HC20}$ 127.3, $^2J_{HC20}$ 2.5–2.8), 166.59 br.s (s) (C^{21}), 62.27 t.q (s) (C^{22}, $^1J_{HC22}$ 148.6, $^2J_{HC22}$ 4.4), 13.18 q.t (s) (C^{23}, $^1J_{HC23}$ 127.7, $^3J_{HC23}$ 2.8–3.0). ^{31}P–{^{1}H} NMR spectrum (CH_2Cl_2): δ_P –25.7 ppm. Mass spec-trum (EI), *m*/*z*: 428 $[M]^{+\bullet}$ (calculated for $C_{19}H_{25}O_9P$ 428), 37 $[M - (CH_3)_2CH{=}CH]^+$, 372 $[M - 2C_2H_4]^+$ $[M - (CH_3)_2CH{=}CH_2]^+$, 371 $[M - C_2H_5 - C_2H_4]^+$, 331 $[M - C_6H_9O]^+$, 330 $[M - C_6H_{10}O]^+$, 257 $[M - C_6H_4O_2P(O)O]^+$, 256 $[M - C_6H_4O_2P(O)OH]^+$, 201 $[M - 2CO_2 - 2C_2H_4 - (CH_3)_2C{=}CH_2CCH_3]^+$ $[C_6H_4O_2PO_2CH_2O]^+$, 173 $[C_6H_4O_2P(OH)_2]^+$, 172 $[C_6H_4O_2P(O)(OH)]^+$, 156 $[C_6H_4O_2POH]^+$, 155 $[C_6H_4O_2PO]^+$, 139 $[C_6H_4O_2P]^+$, 110 $[C_6H_4(OH)_2]^+$, 109 $[C_6H_4O_2H]^+$, 99 $[C_6H_{11}O]^+$, 98 $[C_{6H}10O]^+$, 97 $[C_6H_9O]^+$, 83 $[C_6H_{11}]^+$, 82 $[C_{6H}10]^+$, 81 $[C_6H_9]^+$, 73 $[COOEt]^+$, 58 $[(CH_3)_2CO]^+$, 56 $[(CH_3)_2C{=}CH_2]^+$, 45 $[OEt]^+$, 44 $[CO_2]^+$, 42 $[(CH_3)C{=}CH_2]^+$, 29 $[C_2H_5]^+$, 28 $[C_2H_4]^+$, 28 $[CO]^+$. Found, %: C 53.14; H 6.07. $C_{19}H_{25}O_9P$. Calculated, %: C 53.27; H 5.84.

3,4-Benzo-5-methyl-1,1-phenylenoxydioxy-7,7-bis(ethoxycarbonyl)-2,6,8,1-trioxaphosphabicyclo-[3.2.1^{1,5}]octane (XVIII). A mixture of 3.95 g (0.014 mol) of 2-[2-(methylcarbonyl)-1-phenoxy]-1,3,2-benzodioxaphosphole (**VI**), 2.50 g (0.014 mol) of diethyl mesoxalate, 10 mL CCl_4, and 20 mL of CH_2Cl_2 was incubated during two months and then diluted with 20 mL of hexane. The formed colorless crystals of compound **XVIII** were filtered off and dried in vacuum (10 mm Hg). Yield 5.6 g (90%), mp 64–66°C. IR spectrum, ν, cm^{-1}: 3434, 3064, 3039, 2984, 2936, 2907, 2868, 2615, 1755, 1627, 1613, 1591, 1493, 1462, 1444, 1380, 1358, 1345, 1273, 1215, 1161, 1137, 1091, 1075, 1035, 1007, 987, 948, 934, 885, 871, 857, 837, 820, 792, 772, 759, 740, 696, 680, 671, 644, 622, 603, 549, 529, 455. ^{1}H NMR spectrum (400 MHz, $CDCl_3$), δ, ppm (*J*, Hz): 7.38 d.d (H^{18}, $^3J_{H17H18}$ 7.6–7.7, $^4J_{H16H18}$ 1.5–1.6), 7.32 d.d.d.d (H^{16}, $^3J_{H15H16}$ 7.8, $^3J_{H16H17}$ 7.8, $^4J_{H18H16}$ 1.6, $^5J_{PH16}$ 1.5–1.6), 7.17 br.m and 7.01 br.m ($C_6H_4O_2$), 7.13 d.d.d (H^{17}, $^3J_{H16H17}$ 7.8, $^3J_{H16H17}$ 7.6–7.7, $^4J_{H15H17}$ 1.1), 7.00 br.d (H^{15}, $^3J_{H16H15}$ 7.8), 4.25–4.26 m (OCH_2, AB part of the ABX_3 system, $^3J_{AB}$ 9.9–10.2, $^3J_{AX}$ 7.1, $^3J_{BX}$ 7.1), 4.13 m and 4.18 m (OCH_2, AB part of the ABX_3 system, $^3J_{AB}$ 10.6, $^3J_{AX}$ 7.1, $^3J_{BX}$ 7.1), 1.96 d (H^{19}, $^4J_{PH19}$ 1.9), 1.18 t and 0.90 t ($H^{22,25}$, two X_3 parts of the ABX_3 system, $^3J_{AX}$ 7.1, $^3J_{BX}$ 7.1). ^{13}C NMR spectrum (150.9 MHz, $CDCl_3$), δ_C, ppm (*J*, Hz): 151.06 m (d) (C^3, $^3J_{HC3}$ 10.9, $^3J_{HC3}$ 9.1, $^2J_{PC3}$ 6.2, $^2J_{HC3}$ 4.3, $^4J_{HC3}$ 1.8), 127.97 m (d) (C^4, $^3J_{PC4}$ 3.6), 100.18 m (d) (C^5,

$^3J_{PC5}$ 7.5), 82.80 d (d) (C^7, $^1J_{PC7}$ 150.7), 145.33 br.m and 140.75 br.m (both br.s) (C^9, C^{14}), 110.23 br.d.m (br.m) (C^{10}, $^1J_{HC10}$ 163.0, $^3J_{PC10}$ 11.6–12.0), 120.69 br.d.m (br.s) (C^{11}, $^1J_{HC11}$ 162.0, $^3J_{HC11}$ 8.1), 123.21 br.d.m (br.s) (C^{12}, $^1J_{HC12}$ 162.0), 110.46 br.d.m (br.d) (C^{13}, $^1J_{HC13}$ 162.0–163.0, $^3J_{PC13}$ 16.5), 117.44 d.d.d.d.d (d) (C^{15}, $^1J_{HC15}$ 163.0, $^3J_{PC15}$ 12.5, $^3J_{HC15}$ 8.0, $^2J_{HC15}$ 1.6–1.7, $^4J_{HC15}$ 1.5–1.6), 130.09 d.d.d (s) (C^{16}, $^1J_{HC16}$ 162.8, $^3J_{HC16}$ 8.6, $^2J_{HC16}$ 1.6), 123.40 d.d (s) (C^{17}, $^1J_{HC17}$ 163.0, $^3J_{HC17}$ 7.6), 124.10 d.d.d (s) (C^{18}, $^1J_{HC18}$ 159.3, $^3J_{HC18}$ 8.8, $^2J_{HC18}$ 2.0), 23.42 q.d (d) (C^{19}, $^1J_{HC19}$ 129.2, $^3J_{PC19}$ 4.6), 166.08 t.d (br.s) (C^{20}, $^3J_{HC20}$ 3.0, $^2J_{PC20}$ 0.6), 62.22 t.q (s) ($C^{21,24}$, $^1J_{HC}$ 148.7, $^3J_{HC}$ 4.4), 13.25 q.t (s) (C^{22}, $^1J_{HC22}$ 127.5, $^2J_{HC22}$ 2.6–2.7), 165.37 t (s) (C^{23}, $^3J_{HC23}$ 3.1, $^2J_{PC23}$ 0), 12.83 q.t (s) (C^{25}, $^1J_{HC25}$ 127.6, $^2J_{HC25}$ 2.6–2.7). $^{31}P-\{^1H\}$ NMR spectrum (36.5 MHz, CH_2Cl_2): δ_P –24.1 ppm. Mass spectrum (EI), *m*/*z*: 448 $[M]^{+\bullet}$ (calculated for $C_{21}H_{21}O_9P$ 444), 374 $[M - C(O)OEt - 1H]^+$, 274 $[C_{14}H_{11}O_4P]^+$, 259 $[C_{13}H_8O_4P]^+$, 139 $[C_6H_4O_2P]^+$. Found, %: C 56.44; H 4.77. $C_{21}H_{21}O_9P$. Calculated, %: C 56.25; H 4.68.

X-ray diffraction analysis of compound **XVIII** crystals was performed using a Bruker Smart APEX II CCD automated diffractometer (graphite monochromator, λ MoK_α 0.71073 Å, ω-scanning, 293 K). Semi-empirical absorption corrections were applied using SADABS software [31]. The structure was solved by the direct method using SIR software [32] and refined first isotropically and then anisotropically using the SHELXL-97 software [33] as implemented in the WinGX package [34]. The H^{8A} and H^{8B} atoms were located in from the Fourier difference series and further refined isotropically. The other hydrogen atoms were placed in geometrically calculated positions and refined using a *rider* model. Data collection and processing as well as refinement of the unit cell parameters were performed using APEX2 software [35]. Analysis of intermolecular interactions and drawing were performed using PLATON [30] and ORTEP [36] software.

Crystals of compound **XVIII**, colorless, prismatic, monoclinic, $C_{21}H_{21}O_9P$, M_{calc} 448.35; *a* 8.790(6), *b* 24.25(2), *c* 10.516(7) Å, β 112.101(7)°; *V* 2077(2) Å^3, d_{calc} 1.43 g/cm^3, *Z* 4, space group $P2_1/n$, μ(MoK_α) 1.84 cm^{-1}. Scan range $2.3° < \theta < 26.0°$. Measured 4013 unique reflections, including 3290 with $I \geq 2\sigma$. Final divergence factors *R* 0.0394 and R_w 0.1011 basing on 3290 reflections with $F > 2\sigma(F^2)$.

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