ISSN 1070-3632, Russian Journal of General Chemistry, 2006, Vol. 76, No. 3, pp. 391–411. © Pleiades Publishing, Inc., 2006.
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Dedicated to the 90th Anniversary of Corresponding Member of the Russian Academy of Sciences A.N. Pudovik

Reaction of Trihalo(phenylenedioxy)phosphoranes with Acetylenes: X.[1] Specific Features of the Reactions of Substituted 2,2,2-Trichloro-1,3,2λ^5-benzodioxaphospholes with 3-Chloro(bromo, iodo)propynes

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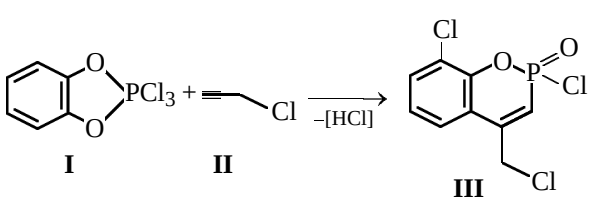
Received March 9, 2005

Abstract — It was shown for the first time that 3-chloro-, 3-bromo-, and 3-iodopropynes can react with 2,2,2-trichloro-, 2,2,2-trichloro-5-methyl-, and 5,6-dibromo-2,2,2-trichloro-1,3,2λ^5-benzodioxaphospholes to give derivatives of 4-(halomethyl)-2-chloro-2*H*-1,2λ^5-benzoxaphosphinin-2-ones. The reaction involves nonselective chlorination of the phenylene substituent in different positions, and the resulting isomer ratio is temperature-dependent. In the reactions of 3-bromo- and 3-iodopropynes with 2,2,2-trichloro-1,3,2λ^5-benzodioxaphosphole, a side process takes place, viz. nucleophilic substitution of bromine and iodine with chlorine. The structure of some of the prepared 4-(chloromethyl)-1,2- benzoxaphosphinines was studied by means of X-ray diffraction.

DOI: 10.1134/S1070363206030091

The reaction of 2,2,2-trichloro-1,3,2λ^5-benzodioxaphosphole (**I**) and some of its derivatives bearing a halogen, methyl, or chlorocarbonyl substituent in the phenylene fragment, with arylacetylenes leads to formation of the heterocyclic system of 1,2-benzoxaphosphinine [1–4], a structural P-analog of natural heterocycles, such as coumarin or α-chromene [7]. Among coumarin or α-chromene derivatives, a great number of highly biologically active compounds have been found [5–9].

In the present research we showed for the first time that such alkylacetylenes as 3-chloro-, 3-bromo- and 3-iodopropynes can be involved in reaction with various derivatives of P,P,P-trichloro-1,3,2-benzodioxaphospholes. Hence, benzophosphole **I** on prolonged (more than 2 months) standing in a solution of excess 3-chloropropyne (**II**) (or in methylene chloride) reacts with preferential formation of a phosphorus-containing compound (60–70%) which gives a ^{31}P NMR signal at δ_P 15.6 ppm (in CH_2Cl_2). This compound fairly easily crystallizes from the reaction mixture and can be isolated. According to ^{1}H and ^{13}C NMR data (see Experimental and Table 1), it is 2,8-dichloro-4-(chloromethyl)-2*H*-1,2λ^5-benzoxaphosphinin-2-one (**III**). The ^{13}C–{^{1}H} NMR spectrum of compound **III** shows an upfield and a downfield signals characteristic of the P–C^{3}H=C^4 fragment [δ, ppm (*J*, Hz): C^3, 115.78 d.d.t.d ($^1J_{PC}$ 156.1, $^1J_{HC}$ 171.6, $^3J_{HCCCC}$ 5.3, $^4J_{HCCCC}$ 2.2); C^4 149.19 m ($^2J_{PCC}$ 2.9 Hz)]. Taking into account that, along with the C^4 signal, the spectrum contains three more signals of carbons bearing no protons (C^{4a}, C^8, C^{8a}), we can state that the chlorine atom enters into the benzo fragment. The carbon chemical shifts and the $^{31}J_{POCC}$ coupling constant of 8.1 Hz for one of the *ipso*-carbon atoms (C^8) made us to conclude that the chlorine atom locates *ortho* with respect to the endocyclic O^1 atom. It is just this atom that the $^4J_{POCC^{8a}}$ constant can reach the mentioned value, whereas for any other carbon atom (C$^{5-7}$) it does not exceed 2 Hz [10].



I **II** **III**

1 For communication IX, see [1].

Table 1. ^{13}C NMR spectral data for the obtained compounds, δ, ppm (*J*, Hz)[a]

Atom	**III** ($CDCl_3$) (45°C)	**III** ($CHCl_3$) (D_2O insert, 25°C)	**IV** (ethanol-d_6) (25°C)
C^3	115.78 d (d.d.t.d)[a] (156.1, PC^3; 171.6, HC^3; 5.3, HC^9CC^3; 2.2, HC^5CCC^3)	116.72 d (d.d.t.d)[a] (156.5, PC^3; 170.9, HC^3; 5.4, HC^9CC^3; 2.1, HC^5CCC^3)	117.42 d (d.d.t) (173.3, PC^3; 164.2, HC^3; 5.2, HC^9CC^3)
C^4	149.19 d (br.m) (3.5–4.2, HCC^4; 3.4–3.6, $H^2C^9C^4$; 2.9, PC^3C^4)	149.49 d (br.m) (3.9, HCC^4; 3.5, $H^2C^9C^4$; 2.9, PC^3C^4)	148.63 d (m) (2.9, PC^3C^4)
C^{4a}	120.15 d (m) (18.1, $PCCC^{4a}$)	120.51 d (m) (18.1, $PCCC^{4a}$)	122.72 d (m) (16.4, $PCCC^{4a}$)
C^5	124.41 d (d.d.d.d) (162.4, HC^5; 8.6, HC^7CC^5; 1.5, HC^6C^5; 1.4, $POCCC^5$)	124.37 d (d.d.d.d) (161.0, HC^5; 8.4, HC^7CC^5; 1.5, HC^6C^5; 1.4, $POCCC^5$)	126.14 d (d.d. d) (162.2, HC^5; 8.6, HC^7CC^5; 1.0, $POCCC^5$)
C^6	124.86 d (br.d) (165.5, HC^6; 1.2, $POCCCC^6$)	125.14 d (br.d) (164.5, HC^6; 1.4, $POCCCC^6$)	124.92 d (d.d) (165.2, HC^6; 0.7, $POCCCC^6$)
C^7	132.68 s (d.d.d) (167.9, HC^7; 8.9, HC^5CC^7; 2.0, HC^6C^7)	133.11 s (d.d. d) (168.4, HC^7; 9.1, HC^5CC^7; 2.0, HC^6C^7)	132.76 s (d.d.d) (166.6, HC^7; 8.9, HC^5CC^7; 2.9, HC^6C^7)
C^8	124.38 d (m) (8.1, $POCC^8$)	125.14 d (m) (10.5–11.0, HC^6CC^8; 8.0, $POCC^8$; 2.9–3.5, HC^7C^8; 1.4, HC^5CCC^8)	125.33 d (m) (7.4, $POCC^8$)
C^{8a}	146.21 d (br.d.d.d) (9.7, POC^{8a}; 10.0–10.3, HC^7CC^{8a}; 10.0–10.3, HC^5CC^{8a})	146.75 d (m) (9.5, POC^{8a}; 10.0–10.5, HC^7CC^{8a}; 10.0–10.5, HC^5CC^{8a})	148.73 d (m) (7.4, POC^{8a})
C^9	43.37 d (t.d.d) (153.3, HC^9; 23.5, PC^3CC^9; 8.2, HC^3CC^9) PC^3CC^9; 8.2, HC^3CC^9)	43.59 d (t.d.d) (153.3, HC^9; 23.6, 21.9, PC^3CC^9; 8.4, HC^3CC^9)	45.55 d (t.d.d) (153.5, HC^9;

Atom	**V** (DMSO–acetone-d_6, 1 : 1, 37°C)[b]	**VII** ($CDCl_3$) (45°C)	**XIII** ($CDCl_3$ (45°C)
C^3	116.84 d (d.d.t) (157.9, PC^3; 163.4, HC^3; 5.4–5.5, HC^9CC^3)	114.80 d (d.d.t.d) (155.8, PC^3; 171.5, HC^3; 5.3, HC^9CC^3; 2.2, HC^5CCC^3)	116.11 d (d.d.t.d) (155.7, PC^3; 171.3, HC^3; 5.2–5.3, HC^9CC^3; 2.3, HC^5CCC^3)
C^4	147.83 d (d.t.d) (5.1, HC^5CC^4; 3.7, $H^2C^9C^4$; 1.8, PC^3C^4)	149.61 d (m) (3.5–4.2, HCC^4; 3.4–3.6, $H^2C^9C^4$; 2.8, PC^3C^4)	148.82 d (br.m) (3.5–4.2, HCC^4; 3.4–3.6, $H^2C^9C^4$; 2.7, PC^3C^4)
C^{4a}	119.80 d (m) (15.2, $PCCC^{4a}$)	117.39 d (m) (18.3, $PCCC^{4a}$)	119.86 d (m) (18.0, $PCCC^{4a}$)
C^5	125.14 s (d.d.d.t) (162.9, HC^5; 8.5, HC^7CC^5; 1.0–1.1, HC^6C^5; 1.0–1.1, H^2CCCC^5)	127.0 d (d.d.d) (162.9, HC^5; 1.6, $POCCC^5$; 1.3, HC^6C^5)	125.72 d (d.d.d.d) (167.3, HC^5; 5.7, HC^7CC^5; 1.5, $HCCCC^5$; 1.5, $POCCC^5$)
C^6	123.22 s (br.d) (166.0, HC^6)	125.24 d (br.d.d) (169.7, HC^6; 5.3, HC^8CC^6; 1.2, $POCCCC^6$)	130.25 d (d.d.d.d.d) (11.3, HC^8CC^6; 5.0, HCC^6; 3.8, HCC^6; 1.4, $HCCCCC^6$; 1.4, $POCCCC^6$)
C^7	131.08 s (d.d.d) (167.7, HC^7; 8.8, HC^5CC^7; 1.9, HC^6C^7)	137.62 d (d.d.d.d) (12.7, HC^5CC^7; 3.9, HCC^7; 3.4, HCC^7; 0.7, $POCCC^7$)	131.95 s (d.d.d) (166.9, HC^7; 6.1, HC^5CC^7; 2.3, HC^8C^7)
C^8	122.43 d (m) (6.9–7.0, $POCC^8$)	119.61 d (d.d.d.d) (170.2, HC^8; 8.6, $POCC^8$; 5.4, HC^6CC^8; 1.1, HC^5CCC^8)	120.72 d (d.d.d.d) (165.3, HC^8; 8.4, $POCC^8$; 3.3, HC^7C^8)
C^{8a}	146.99 d (d.d.d.d) (9.5–9.7, HC^7CC^{8a}; 9.5–9.7, HC^5CC^{8a}; 9.7, POC^{8a}; 1.5, HC^6CCC^{8a})	150.62 d (d.d. d) (10.5–10.8, HC^5CC^{8a}; 10.1, POC^{8a}; 5.0–5.2, HC^8C^{8a})	148.78 d (m) (10.3, POC^{8a}; 9.5–9.7, HC^7CC^{8a}; 9.5–9.7, HC^5CC^{8a})
C^9	44.14 d (t.d.d) (154.5, HC^9; 21.2, PC^3CC^9; 8.3, HC^3CC^9)	43.21 d (t.d.d) (152.7, HC^9; 23.4, PC^3CC^9; 7.8, HC^3CC^9)	43.12 d (t.d.d) (152.6, HC^9; 23.2, PC^3CC^9; 7.9, HC^3CC^9)

Table 1. (Contd.)

Atom	**IX** ($CDCl_3$) (45°C)	**XI** (ethanol-d_6) (25°C)	**XIII** ($CDCl_3$ (30°C)
C^3	114.75 d (d.d.t.d) (155.8, PC^3; 170.2, HC^3; 5.3, HC^9CC^3; 2.2, HC^5CCC^3)	118.06 d (d.d.t) (172.3, PC^3; 164.7, HC^3; 4.4, HC^9CC^3)	116.25 d (d.d.t) (155.6, PC^3; 171.0, HC^3; 5.6–5.7, HC^9CC^3)
C^4	149.85 d (br.m) (3.5–4.2, HCC^4; 3.4, $H^2C^9C^4$; 3.0, PC^3C^4)	147.07 s (m)	149.96 d (m) (2.4, PC^3C^4)
C^{4a}	118.57 d (m) (18.0, $PCCC^{4a}$)	122.12 d (m) (15.3, $PCCC^{4a}$)	120.12 d (m) (17.3, $PCCC^{4a}$)
C^5	124.86 d (br.d.d) (164.4, HC^5; 8.7, HC^7CC^5; 1.2, $POCCC^5$)	126.70 s (d.d) (164.8, HC^5; 5.8, HC^7CC^5)	124.92 d (br.d.d) (161.3, HC^5; 6.5, HC7CC5; 1.5, $POCCC^5$)
C^6	124.86 d (br.d.d) (164.4, HC^6; 8.7, HC^8CC^6; 1.2, $POCCCC^6$)	129.43 s (d.d.d) (11.0, HC^8CC^6; 4.5, HCC^6; 4.4–4.5, HCC^6)	124.97 d (br.d) (165.1, HC^6; 1.3, $POCCCC^6$)
C^7	132.27 s (d.d) (163.7, HC^7; 8.7, HC^5CC^7)	131.67 s (d.d) (167.3, HC^7; 6.8, HC^5CC^7)	132.94 s (d.d.d) (167.8, HC^7; 8.9, HC^5CC^7; 2.0, HC^6C^7)
C^8	119.30 d (d.d.d.d) (164.8, HC^8; 9.8, HC^6CC^8; 8.3, $POCC^8$; 3.3, HC^7C^8; 1.8, HC^5C^8	121.77 d (d.d) (164.5, HC^8; 6.8, $POCC^8$)	124.64 d (m) (8.2, $POCC^8$)
C^{8a}	150.35 d (m) (10.3, POC^{8a})	151.08 d (m) (6.5, POC^{8a})	146.52 d (d.d.d) (9.5, POC^{8a}; 9.5–9.6, $HCCC^{8a}$; 7.9–8.0, $HCCC^{8a}$)
C^9	43.36 d (t.d.d) (152.9, HC9; 23.5, PC^3CC^9; 7.8, HC^3CC^9)	45.15 d (t.d.d) (153.3, HC^9; 22.3, PC^3CC^9; 8.1, HC^3CC^9)	29.50 d (t.d.d) (154.9, HC^9; 25.0, PC^3CC^9; 8.2, HC^3CC^9)

Atom	**XIV** ($CDCl_3$) (30°C)	**XV** ($CDCl_3$) (30°C)	**XVI** ($CDCl_3$ (30°C)
C^3	115.39 d (d.d.t) (155.8, PC^3; 170.0, HC^3; 5.6–5.7, HC^9CC^3)	116.55 d (d.d.t) (155.2, PC^3; 170.4, HC^3; 5.6–5.7, HC^9CC^3)	115.31 d (d.d.t) (155.7, PC^3; 171.0, HC^3; 5.6–5.7, HC^9CC^3)
C^4	149.61 d (m) (2.9, PC^3C^4)	149.18 d (m) (2.3, PC^3C^4)	150.24 d (m) (2.7, PC^3C^4)
C^{4a}	117.21 d (m) (17.9, $PCCC^{4a}$)	119.84 d (m) (17.6, $PCCC^{4a}$)	118.52 d (m) (17.6, $PCCC^{4a}$)
C^5	127.49 d (d.m) (164.5, HC^5; 1.5, $POCCC^5$)	126.22 d (d.d.d) (165.9, HC^5; 6.7, HC^7CC^5; 1.5, $POCCC^5$)	126.44 d (br.d.m) (162.0, HC^5; 7.9, HC^7CC^5; 1.4, $POCCC^5$)
C^6	125.37 d (d.d.d) (168.5, HC^6; 4.0–4.3, HC^8CC^6; 1.2, $POCCCC^6$)	130.38 d (d.m) (11.5, HC^8CC^6; 3.8, HCC^6; 3.8, HCC^6; 1.4, $HCCCC^6$)	125.03 d (br.d.d) (165.3, HC^6; 5.8, HC^8CC^6; 1.4, POCCCC6)
C^7	137.88 s (d.d.d) (11.8, HC^5CC^7; 3.0, HCC^7; 3.0, HCC^7)	132.19 s (d.d) (167.6, HC^7; 5.8, HC^5CC^7)	132.49 s (d.d) (163.5, HC^7; 9.0, HC^5CC^7)
C^8	119.86 d (d.d.d) (168.7, HC^8; 8.5, $POCC^8$; 5.6, HC^6CC^8)	120.93 d (d.d), 167.8, HC^8; 8.5, $POCC^8$)	119.53 d (d.d.d) (165.1, HC^8; 8.3, POCC8; 5.7, HC6CC8)
C^{8a}	150.92 d (m) (10.3, POC^{8a})	149.07 d (m) (10.3, POC^8)	150.67 d (m) (10.5, POC^{8a})
C^9	29.40 d (t.d.d) (154.8, HC^9; 25.0, PC^3CC^9; 8.2, HC^3CC^9)	29.40 d (t.d.d) (154.2, HC^9; 24.7, PC^3CC^9; 8.5, HC^3CC^9)	29.56 d (t.d.d) (155.8, HC^9; 24.9, PC^3CC^9; 8.1, HC^3CC^9)

Atom	**XXIa** (DMSO-d_6) (40°C)	**XXIIa** (DMSO-d_6) (40°C)
C^3	114.86 d (d.d.t) (170.5, PC^3; 166.0, HC^3; 4.4, HC^9CC^3)	114.94 d (d.d.t) (169.7, PC^3; 166.0, HC^3; 4.4, HC^9CC^3)
C^4	146.81 d (m) (5.6, PC^3C^4)	149.36 d (m) (4.8, PC^3C^4)
C^{4a}	123.29 d (m) (17.3, $PCCC^{4a}$)	123.38 d (m) (18.2, $PCCC^{4a}$)
C^5	125.24 s (d.d) (162.0, HC^5; 7.8–8.0, HC^7CC^5)	125.76 c (d.d) (165.3, HC^5; 5.2, HC^7CC^5)
C^6	123.77 s (d) (165.0, HC^6)	127.56 s (d.d. d) (12.9–13.1, HC^8CC^6; 3.9–4.0, HCC^6; 2.8–3.0, HCC^6)
C^7	130.91 s (d.d) (167.3, HC^7; 8.5, HC^5CC^7)	130.31 s (d.d) (166.7, HC^7; 4.7, HC^5CC^7)
C^8	122.80 d (m) (5.8, $POCC^8$)	126.87 d (d.d) (164.3, HC^8; 6.8, $POCC^8$)
C^{8a}	150.0 d (m) (7.1, POC^{8a})	149.74 d (m) (7.2, POC^{8a})
C^9	31.77 d (m) (19.3, PC^3CC^9)	31.08 d (m) (153.3, HC^9; 19.7, PC^3CC^9; 8.1, HC^3CC^9)

Table 1. (Contd.)

Atom	**XXIV** ($CDCl_3$) (crystal im mixture with **XXV**, 30°C)	**XXIV** [bp 180–187°C (0.1 mm Hg), 30°C, $CDCl_3$, *c* 45%] (glassy material before distillation, *c* 20%)[d]	**XXV** ($CDCl_3$) (crystals in mixtures with **XXIV**, 30°C)
C^3	115.36 d (d.d.t) (156.4, PC^3; 171.3, HC^3; 5.2, HC^9CC^3)	115.15 d (d.d.t) (156.0, PC^3; 170.2, HC^3; 5.0–5.3, HC^9CC^3) [114.88 d (d.d.t) (156.0, PC^3; 171.7, HC^3; 5.6, HC^9CC^3)]	114.87 d (d.d.t) (157.0, PC^3; 171.3, HC^3; 5.3, HC^9CC^3)
C^4	149.22 d (m) (2.9, PC^3C^4)	148.98 d (m) (3.3, PC^3C^4) [149.26 d (m) (2.9, PC^3C^4)]	150.09 d (m) (3.2, PC^3C^4)
C^{4a}	118.08 d (m) (18.3, $PCCC^{4a}$)	117.86 d (m) (18.4, $PCCC^{4a}$) [117.76 d (m) (18.4, $PCCC^{4a}$)]	118.14 d (m) (18.0, $PCCC^{4a}$)
C^5	126.22 br.s (br.d) (164.8, HC^5)	126.02 d (br.d) (164.6, HC^5; 1.3, $POCCC^5$) [126.06 d (br.d) (165.1, HC^5; 1.3, $POCCC^5$)]	123.56 br.s (br.d) (162.0, HC^5)
C^6	130.98 br.s (br.d.q.d) (10.5, HC^8CC^6; 5.2, $H^3CC^7C^6$; 5.1, HCC^6)	130.69 d (br.d.q.d) (10.5, HC^8CC^6; 5.2, $H^3CC^7C^6$; 5.1, HCC^6; 1.1, $POCCCC^6$) [130.64 d (br.d.q.d) (10.4, HC^8CC^6; 5.2, $H^3CC^7C^6$; 5.2, HCC^6; 1.2, $POCCCC^6$)]	126.57 br.s (br.d. q) (161.7, HC^6; 5.2, $H^3CC^7C^6$)
C^7	141.70 s (d.q) (6.3, HC^5CC^7; 6.3, H^3CC^7)	141.86 s (d.q) (6.0, HC^5CC^7; 6.0, H^3CC^7) [141.41 s (d. q) (6.3, HC^5CC^7; 6.2, H^3CC^7)]	142.16 s (d.q) (6.8, HC^5CC^7; 5.8, H^3CC^7)
C^8	121.83 d (d.d.q) (165.2, HC^8; 8.3, $POCC^8$; 5.3, $HC^3C^7C^8$)	121.53 d (d.d.q) (165.2, HC^8; 8.3, $POCC^8$; 4.9–5.1, $HC^3C^7C^8$) [121.47 d (d.d.q) (165.3, HC^8; 8.3, $POCC^8$; 4.8–5.1, $HC^3C^7C^8$)]	125.07 d (m) (8.1, $POCC^8$)
C^{8a}	149.02 d (d.d.d) (10.2, POC^{8a}; 10.2, HC^5CC^{8a}; 4.5, $HC8C^{8a}$)	148.80 d (d.d.d) (10.1, POC^{8a}; 10.2, HC^5CC^{8a}; 4.2, HC^8C^{8a}) 148.65 d (d.d.d) (10.1, POC^{8a}; 10.2, $HC5CC^{8a}$; 4.0, $HC8C^{8a}$)]	146.84 d (d.d) (9.5, POC^{8a}; 9.5, $HC5CC^{8a}$)
C^9	43.51 d (t.d.d) (152.3, HC^9; 23.4, PC^3CC^9; 7.7, HC^3CC^9)	43.24 d (t.d.d) (153.0, HC^9; 23.5, PC^3CC^9; 7.9, HC^3CC^9) [43.33 d (t.d.d) (152.7, HC^9; 24.0, PC^3CC^9; 7.7, HC^3CC^9)]	43.74 d (t.d.d) (152.4, HC^9; 24.0, PC^3CC^9; 7.7, HC^3CC^9)

Atom	**XXV** [bp 180–187°C (0.1 mm Hg), 30°C, $CDCl_3$, *c* 45%] (glassy material befor distillation, *c* 20%)[f]	**XXVI** ($CDCl_3$) [bp 180–187°C (0.1 mm Hg), 30°C, $CDCl_3$, *c* 45%] (glassy material befor distillation, *c* 20%)[g]
C^3	115.63 d (d.d.t) (157.1, PC^3; 171.1, HC^3; 5.3, HC^9CC^3) [114.33 d (d.d.t) (156.2, PC^3; 171.7, HC^3; 5.4, HC^9CC^3)]	115.56 d (d.d.t) (157.6, PC^3; 172.4, HC^3; 5.0–5.2, HC^9CC^3) [115.25 d (d.d.t) (155.0, PC^3; 171.2, HC^3; 5.1, HC^9CC^3)]
C^4	149.94 d (m) (2.7, PC^3C^4) [150.17 d (m) (3.2, PC^3C^4)]	149.56 d (m) (3.0, PC^3C^4) [149.78 d (m) (3.0, PC^3C^4)]
C^{4a}	117.93 d (m) (18.1, $PCCC^{4a}$) [117.82 d (m) (18.0, $PCCC^{4a}$)]	118.91 d (m) (18.2, $PCCC^{4a}$) [118.83 d (m) (18.0, $PCCC^{4a}$)]
C^5	123.38 d (br.d) (161.7, HC^5; 1.2, $POCCC^5$) [123.53 d (br.d) (162.4, HC^5; 1.3, $POCCC^5$)]	126.14 br.s (d.d.t) (160.5, HC^5; 6.2, HC^7CC^5; 5.3–5.4, H^2CCC^5) [126.29 br.s (d.t) (161.0, HC^5; 6.0–6.1, HC^7CC^5; 5.2, H^2CCC^5)]
C^6	126.32 br.s (br.d. q) (161.0, HC^6; 5.2, $H^3CC^7C^6$) [126.40 br.s (br.d.q) (163.0, HC^6; 5.0, $H^3CC^7C^6$)]	135.30 d (br.d.t) (7.7, HC^8CC^6; 4.3, H^2CC^6; 1.2, $POCCCC^6$) [134.68 d (br.d.t) (7.8, HC^8CC^6; 4.0, H^2CC^6; 1.1, $POCCCC^6$)]

Table 1. (Contd.)

Atom	**XXV** [bp 180–187°C (0.1 mm Hg), 30°C, $CDCl_3$, *c* 45%] (glassy material befor distillation, *c* 20%)[f]	**XXVI** ($CDCl_3$) [bp 180–187°C (0.1 mm Hg), 30°C, $CDCl_3$, *c* 45%] (glassy material befor distillation, *c* 20%)[g]
C^7	141.41 s (d. q) (8.3, HC^5CC^7; 6.2, H^3CC^7) [141.83 s (d.q) (8.4, HC^5CC^7; 6.0–6.1, H^3CC^7)]	132.45 br.s (br.d.d.t) (162.1, HC^7; 7.6, HC^5CC^7; 4.8, H^2CCC^7) [132.56 br.s (br.d.d.t) (162.7, HC^7; 7.5, HC^5CC^7; 4.7, H^2CCC^7)]
C^8	124.72 d (m) (8.2, $POCC^8$) [124.51 d (m) (8.0, $POCC^8$)]	119.91 d (d.d) (166.1, HC^8; 8.3, $POCC^8$) [119.84 d (d.d) (166.0, HC^8; 8.3, $POCC^8$)]
C^{8a}	146.59 d (d.d) (9.5, POC^{8a}; 9.5, HC^5CC^{8a}) [146.39 d (d.d)	150.31 d (d.d.d.d) (10.2, POC^{8a}; 10.3, HC^5CC^{8a}; 10.3, HC^7CC^{8a}; 4.7, $HC8C^{8a}$) [150.14 d (d.d.d.d) (10.1, POC^{8a}; 10.2, HC^5CC^{8a}; 10.2, HC^7CC^{8a}; 4.4, HC^8C^{8a})]
C^9	43.40 d (t.d.d) (152.5, HC^9; 23.1, PC^3CC^9; 7.8, HC^3CC^9) [43.49 d (t.d.d) (152.6, HC^9; 23.3, PC^3CC^9; 7.7, HC^3CC^9)]	43.48 d (t.d.d) (152.8, HC^9; 23.7, PC^3CC^9; 7.7, HC^3CC^9) [43.57 d (t.d.d) (153.1, HC^9; 24.0, PC^3CC^9; 7.9, HC^3CC^9)]

Atom	**XXVII** [bp 180–187°C (0.1 mm Hg), 30°C, $CDCl_3$, *c* 45%] (glassy material befor distillation, *c* 20%)[h]	**XXVIII** ($CDCl_3$) [bp 180–187°C (0.1 mm Hg), 30°C, $CDCl_3$, *c* 45%] (glassy material befor distillation, *c* 20%)[i]
C^3	115.86 d (d.d.t) (155.6, PC^3; 169.9, HC^3; 5.3, HC^9CC^3) [115.55 d (d.d.t) (156.4, PC^3; 171.4, HC^3; 5.4, HC^9CC^3)]	113.78 d (d.d.t) (156.9, PC^3; 170.0, HC^3; 5.3, HC^9CC^3) [113.46 d (d.d.t) (156.5, PC^3; 170.0, HC^3; 5.2, HC^9CC^3)]
C^4	149.81 d (m) (2.9, PC^3C^4) [150.04 d (m) (2.9, PC^3C^4)]	150.07 d (m) (3.3, PC^3C^4) [150.21 d (m) (3.0, PC^3C^4)]
C^{4a}	120.01 d (m) (18.0, $PCCC^{4a}$) [119.89 d (m) (18.0, $PCCC^{4a}$)]	116.25 d (m) (18.2, $PCCC^{4a}$) [116.12 d (m) (18.4, $PCCC^{4a}$)]
C^5	124.80 d (br.d.m) (160.7, HC^5; 6.3–6.5, HC^7CC^5; 5.3, $H^3CC^6C^5$; 1.3, $POCCC^5$) [124.95 d (br.d.m) (159.5, HC^5; 6.5–6.6, HC^7CC^5; 5.0–5.3, $H^3CC^6C^5$; 1.2, $POCCC^5$)]	125.72 d (br.d) (159.8, HC^5; 1.3, $POCCC^5$) [125.80 d (br.d) (160.3, HC^5; 1.1, $POCCC^5$)]
C^6	134.69 d (m) (4.8, H^3CC^6; 4.8–5.0, HCC^6; 1.2, $POCCCC^6$) [135.38 d (br.q.d) (4.8–5.0, H^3CC^6; 4.8–5.0, HCC^6; 1.4, $POCCCC^6$)]	125.91 s (d.q) (167.5, HC^6; 6.6, HC^8CC^6; 5.4, $H^3CC^7C^6$) [125.98 br.s (br.d.m) (167.0, HC^6)]
C^7	133.33 s (d.d.q) (165.7, HC^7; 7.5, HC^5CC^7; 5.3, H^3CCC^7) [133.30 s (d.d.q) (165.8, HC^7; 7.6–7.7, HC^5CC^7; 5.2, H^3CC^7)]	143.90 s (d.q) (8.6, HC^5CC^7; 6.0, H^3CC^7) [143.92 s (m) (8.8, HC^5CC^7; 6.0, H^3CC^7)]
C^8	124.14 d (m) (8.0, $POCC^8$) [123.90 d (d.d. d) (8.1, $POCC^8$; 4.4, HC^7C^8; 1.4, HC^5CCC^8)]	119.83 d (d.m) (165.0, HC^8; 8.3, $POCC^8$) [119.74 d (d.m) (165.3, HC^8; 8.5, $POCC^8$)]
C^{8a}	144.35 d (d.d.d) (9.3, POC^{8a}; 9.6, HC^5CC^{8a}; 9.6, HC^7CC^{8a}) [144.16 d (d.d.d) (9.3, POC^{8a}; 9.3–9.5, HC^5CC^{8a}; 9.3–9.5, HC^7CC^{8a})]	150.59 d (d.d.d) (9.9, POC^{8a}; 10.2, HC^5CC^{8a}; 3.8, HC^8C^{8a}) [150.41 d (d.d.d) (10.1, POC^{8a}; 10.1, HC^5CC^{8a}; 4.0, HC^8C^{8a})]
C^9	43.47 d (t.d.d) (152.8, HC^9; 23.7, PC^3CC^9; 7.7, HC^3CC^9) [43.55 d (t.d.d) (153.0, HC^9; 23.4, PC^3CC^9; 7.8, HC^3CC^9)]	43.24 d (t.d.d) (152.6, HC^9; 24.4, PC^3CC^9; 7.8, HC^3CC^9) [43.57 d (t.d.d) (153.0, HC^9; 24.4, PC^3CC^9; 7.8, HC^3CC^9)]

Atom	**XXIX** [bp 190–187°C (0.1 mm Hg), 30°C, $CDCl_3$, *c* 45%][j]	**XXX** [bp 190–187°C (0.1 mm Hg), 30°C, $CDCl_3$, *c* 45%][k]	**XXXI** (DMSO-d_6) (50°C)[l]
C^3	114.64 d (d.d.t) (156.5, PC^3; 171.4, HC^3; 5.0–5.1, HC^9CC^3)	119.79 d (d.d.t) (159.8, PC^3; 171.7, HC^3; 5.2, HC^9CC^3)	117.02 d (d.d.t) (168.0, PC^3; 164.6, HC^3; 5.0, HC^9CC^3)
C^4	150.27 d (m) (3.4, PC^3C^4)	151.98 d (t.d.d) (4.5–5.0, H_2CC^4; 3.9–4.0, HC^3C^4; 1.8, PC^3C^4)	145.60 d (m) (2.2, PC^3C^4)
C^{4a}	118.38 d (m) (17.7, $PCCC^{4a}$)	120.20 d (m) (18.3, $PCCC^{4a}$)	118.84 d (m) (16.4, $PCCC^{4a}$)

Table 1. (Contd.)

Atom	**XXIX** [bp 190–187°C (0.1 mm Hg), 30°C, $CDCl_3$, *c* 45%][j]	**XXX** [bp 190–187°C (0.1 mm Hg), 30°C, $CDCl_3$, *c* 45%][k]	**XXXI** (DMSO-d_6) (50°C)[l]
C^5	126.18 d (d.m) (1.3, $POCCC^5$)	135.99 s (d.q) (9.5–10.0, HC^7CC^5; 4.5–5.0, H^3CCC^5)	126.33 br.s (br.d) (164.9, HC^5)
C^6	134.88 d (m) (7.2–7.3, HC^8CC^6; 5.8, H^3CC^6; 1.3, $POCCCC^6$)	135.51 d (m) (1.5, $POCCCC^6$)	127.83 s (d.q.d) (10.6, HC^8CC^6; 4.7–5.0, $H^3CC^7C^6$; 4.7–5.0, HC^5C^6)
C^7	133.13 s (d.d.q) (162.5, HC^7; 7.4, HC^5CC^7; 4.7–5.0, H^3CCC^7)	133.43 s (d.q) (163.7, HC^7; 5.0–5.1, H^3CCC^7)	139.02 s (d.q) (5.6, HC^5CC^7; 5.4–5.5, H^3CC^7)
C^8	121.47 d (d.d) (158.0, HC^8; 8.3, $POCC^8$)	118.31 d (d.d.d) (166.6, HC^8; 7.4, $POCC^8$; 1.4, HC^7C^8)	121.39 d (d.d.q) (163.0, HC^8; 5.8, $POCC^8$; 4.5, $H^3CC^7C^8$)
C^{8a}	148.67 d (d.d.d.d) (10.5, POC^{8a}; 10.3–10.5, $HCCC^{8a}$; 9.7–10.0, $HCCC^{8a}$; 4.3–4.5, HC^8C^{8a})	148.87 d (d.d.d) (10.4, POC^{8a}; 10.4, HC^7CC^{8a}; 4.7–4.9, HC^8C^{8a})	149.72 d (d.d.d) (7.3, POC^{8a}; 7.5, HC5CC^{8a}; 3.6, HC8C^{8a})
C^9	43.48 d (t.d.d) (152.8, HC^9; 23.7, PC^3CC^9; 7.7, HC^3CC^9)	46.39 d (t.d.d) (155.3, HC^9; 21.6, PC^3CC^9; 8.1, HC^3CC^9)	44.38 d (t.d.d) (153.7, HC^9; 21.2, PC^3CC^9; 7.9, HC^3CC^9)

Atom	**XXXII** (DMSO-d_6) (50°C)	**XXXVII** (DMSO-d_6) (50°C)
C^3	116.51 d (d.d.t) (169.9, PC^3; 166.0, HC^3; 5.0, HC^9CC^3)	119.23 d (d.d.t) (167.8, PC^3; 163.0, HC^3; 5.6, HC^9CC^3)
C^4	149.39 d (m) (2.3, PC^3C^4)	144.43 br.s (m)
C^{4a}	118.79 d (m) (15.8, $PCCC^{4a}$)	120.80 d (m) (16.5, $PCCC^{4a}$)
C^5	122.27 br.s (d) (162.4, HC^5)	130.61 s (d) (168.5, HC^5)
C^6	124.78 br.s (br.d.q) (159.0, HC^6; 4.5, H^3CCC^6)	117.64 s (d.d) (8.9, HC^8CC^6; 4.6, HC^5C^6)
C^7	139.34 s (d.q.d) (8.3, HC^5CC^7; 5.5, H^3CC^7; 2.0, HC^6C^7)	125.39 s (d.d) (10.1, HC^5CC^7; 4.2, HC^8C^7)
C^8	123.10 d (m) (6.9, $POCC^8$)	124.10 d (d.d) (169.8, HC^8; 7.1, $POCC^8$)
C^{8a}	147.08 d (d.d) (7.7, HC^5CC^{8a}; 6.8, POC^{8a})	150.70 d (d.d.d) (10.2, HC^5CC^{8a}; 7.4, POC^{8a}; 4.8–5.0, HC8C^{8a})
C^9	44.58 d (t.d.d) (155.0, HC^9; 21.7, PC^3CC^9; 7.6, HC^3CC^9)	44.26 d (t.d.d) (154.0, HC^9; 21.2, PC^3CC^9; 8.6, HC^3CC^9)

Atom	**XXXVIII** (DMSO-d_6) (50°C)	**XXXIX** (DMSO-d_6) (50°C)
C^3	119.27 d (d.d.t) (167.8, PC^3; 162.6, HC^3; 5.6, HC^9CC^3)	120.34 d (d.d.t) (168.1, PC^3; 164.3, HC^3; 4.5, HC^9CC^3)
C^4	144.49 br.s (m)	144.13 br.s (m)
C^{4a}	120.59 d (m) (16.1, $PCCC^{4a}$)	121.34 d (m) (16.3, $PCCC^{4a}$; 8.6, HC^3CC^{4a}; 4.4, HC^5C^{4a}; 3.6, H^2CCC^{4a})
C^5	127.40 s (d) (167.9, HC^5)	128.65 s (d) (170.5, HC^5)
C^6	122.94 s (d.d) (9.5, HC^8CC^6; 4.4, HC^5C^6)	118.21 s (d) (4.8, HC^5C^6)
C^7	127.63 s (d.d) (9.5, HC^5CC^7; 4.8–5.0, HC^8C^7)	126.64 s (d) (9.6, HC^5CC^7)
C^8	124.14 d (d.d) (170.0, HC^8; 7.0, $POCC^8$)	125.51 d (d.d) (6.6, $POCC^8$; 1.6, HC^5CCC^8)
C^{8a}	150.18 d (d.d.d) (11.0, HC^5CC^{8a}; 7.4, POC^{8a}; 6.0, HC8C^{8a})	147.17 d (d.d) (10.4, HC^5CC^{8a}; 6.7, POC^{8a})
C^9	44.25 d (t.d.d) (153.5, HC^9; 21.2, PC^3CC^9; 8.6, HC^3CC^9)	44.29 d (t.d.d) (154.8, HC^9; 21.2, PC^3CC^9; 8.1, HC^3CC^9)

[a] The shape of the ^{13}C NMR signal is given in parentheses. [b] $N(CH_2CH_3)_2$, CH_2, δ_C 38.40 d (t.d.q) (137.6, HC; 5.2, PNC; 4.6, HCC); CH_3, δ 13.87 d (q.t.d) (126.3, HC; 2.6, HCC; 1.8, PNCC). [c] CH_3, 20.23 s (q.d) (130.1, HC; 4.6, HC^8CC). [d] CH_3, 19.88 s (q.d) (128.9, HC; 4.6, HC^8CC) [19.96 s (q.d) (129.4, HC; 4.5, HC^8CC)]. [e] CH_3, 20.49 s (q.d) (128.8, HC; 4.6, HC^6CC). [f] CH_3, 20.13 s (q.d) (129.3, HC; 5.0, HC^6CC) [20.20 s (q.d) (129.0, HC; 4.4, HC^6CC)]. [g] $ClCH_2$, 44.59 s (t.d.d) (151.7, HC; 4.9–5.0, HC^5CC; 4.9–5.0, HC^7CC) [44.66 s (t.d.d) (151.0, HC; 4.8, HC^5CC; 4.8, HC^7CC)]. [h] CH_3, 20.44 s (q.d.d) (127.7, HC; 4.4, HC^5CC; 4.4, HC^6CC) [20.48 s (q.d.d) (127.8, HC; 4.4, HC^5CC; 4.4, HC^6CC)]. [i] CH_3, 21.04 s (q.d.d) (127.8, HC; 5.0, HC^6CC; 5.0, HC^8CC) [21.11 s (q.d.d) (127.6, HC; 4.8, HC^6CC; 4.8, HC^8CC)]. [j] CH_3, 20.57 s (q.d.d) (127.3, HC; 4.5, HC^5CC; 4.5, HC^7CC). [k] CH_3, 20.68 s (q.d) (128.9, HC; 4.5, HC^7CC). [l] CH_3, 19.45 s (q.d) (128.8, HC; 4.5, HC^8CC). [m] CH_3, 19.89 s (q.d) (128.0, HC; 4.0, HC^6CC).

Table 2. Selected bond lengths (*d*, Å) and bond (ω, deg) and torsion angles (τ, deg) in compound **III**

Bond	*d*	Bond	*d*	Bond	*d*
Cl^2–P^2	2.020(2)	O^1–C^{8a}	1.395(4)	C^{4a}–C^5	1.414(4)
Cl^7–C^7	1.730(4)	C^3–C^4	1.363(5)	C^{8a}–C^8	1.359(6)
Cl^{12}–C^{12}	1.774(4)	C^3–H^3	0.81(5)	C^8–C^7	1.400(5)
P^2–O^1	1.586(4)	C^4–C^{4a}	1.462(6)	C^6–C^7	1.372(6)
P^2–O^2	1.455(3)	C^4–C^9	1.498(5)	C^5–C^6	1.380(7)
P^2–C^3	1.725(4)	C^{4a}–C^{8a}	1.401(6)	C^9–H^{91}	0.93(4)
Angle	**ω**	**Angle**	**ω**	**Angle**	**ω**
$Cl^2P^2O^1$	103.3(1)	$C^3C^4C^{4a}$	121.3(4)	$Cl^8C^8C^{8a}$	120.4(2)
$Cl^2P^2O^2$	110.4(2)	$C^3C^4C^9$	122.2(4)	$Cl^8C^8C^7$	119.5(3)
$Cl^2P^2C^3$	106.4(2)	$C^5C^4C^9$	116.4(3)	$C^{8a}C^8C^7$	120.1(4)
$O^1P^2O^2$	113.0(2)	$C^4C^{4a}C^{8a}$	121.4(3)	$C^6C^7C^8$	118.8(4)
$O^1P^2C^3$	104.5(2)	$C^4C^{4a}C^5$	121.4(4)	$C^5C^6C^7$	121.8(3)
$O^2P^2C^3$	118.1(2)	$C^{8a}C^{4a}C^5$	117.2(4)	$C^{4a}C^5C^6$	119.9(4)
$P^2O^1C^{8a}$	122.5(3)	$O^1C^{8a}C^{4a}$	121.2(4)	$Cl^9C^9C^4$	113.5(3)
$P^2C^3H^3$	118(3)	$O^1C^{8a}C^8$	116.5(3)	$C^{4a}C^{8a}C^8$	122.2(3)
Angle	**τ**	**Angle**	**τ**	**Angle**	**τ**
$Cl^2P^2O^1C^6$	–79.3(3)	$O^2P^2C^3C^4$	–146.1(3)	$C^3C^4C^{4a}C^{8a}$	13.2(7)
$O^2P^2O^1C^{8a}$	161.4(3)	$P^2O^1C^{8a}C^{4a}$	–24.3(6)	$C^3C^4C^{4a}C^5$	–168.2(4)
$C^3P^2O^1C^{8a}$	31.8(4)	$P^2O^1C^{8a}C^8$	158.1(3)	$C^9C^4C^{4a}C^{8a}$	–166.4(4)
$Cl^2P^2C^3C^4$	89.3(4)	$P^2C^3C^4C^{4a}$	–0.4(6)	$C^9C^4C^{4a}C^5$	12.1(6)
$O^1P^2C^3C^4$	–19.5(4)	$P^2C^3C^4C^9$	179.2(3)	$C^3C^4C^9Cl^9$	–0.2(6)

The structure of phosphinine **III** was also established by means of X-ray diffraction. Table 2 lists selected molecular parameters of this compound (bond lengths and bond and torsion angles). A general view of the molecule in crystal is given in Fig. 1.

As seen from the figure, the chlorine atom is really located *ortho* the endocyclic oxygen atom of the phosphinine heteroring which contains two planar [within 0.005(4) and 0.002(4) Å, respectively] $C^4C^{4a}C^{8a}O^1$ and $P^2C^3C^4C^{4a}$ fragments. The P^2 and C^3 atoms deviate from the $C^4C^{4a}C^{8a}O^1$ plane by 0.531(1) and 0.247(4) Å, respectively. The C^{8a} and O^1 atoms deviate from the second planar fragment to one side but by different distances [–0.465(4) and –0.520(3) Å, respectively]. These data show that the heteroring conformation is unsymmetric *boat*. The planar phosphinine fragments are turned about the C^4–C^{4a} bond by 11.2(6)°. Note that the Cl^9 atom, too, is located in the $P^2C^3C^4C^{4a}$ plane [C^3–C^4 is almost eclipsing C^9–Cl^9; $C^3C^4C^9Cl^9$ torsion angle –0.2(6)°]. The phosphorus atom has a distorted tetrahedral coordination. The chlorine atom on phosphorus is axial [it deviates from the $C^4C^{4a}C^{8a}O^1$ and $P^2C^3C^4C^{4a}$ planes by 2.573(1) and 1.938(1) Å, respectively], and the phosphoryl group has an equatorial location [O^2 deviates from the $C^4C^{4a}C^{8a}O^1$ plane by 0.107(3) Å and from the $P^2C^4C^4C^{4a}$ plane by –0.715(3) Å], which is probably determined by the anomeric effect of the endocyclic oxygen atom. Under these conditions, a

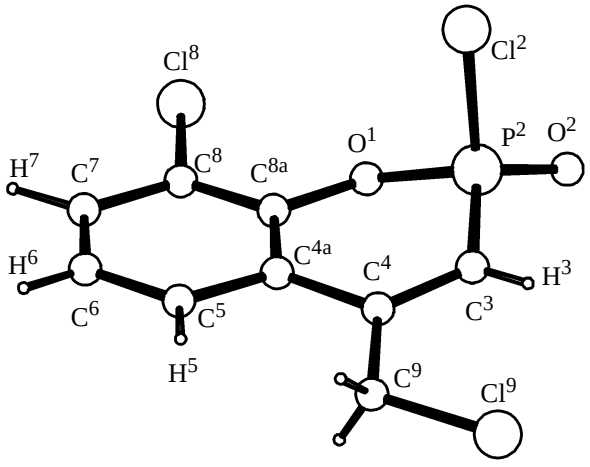


Fig. 1. General view of a molecule of phosphinine **III** in crystal.

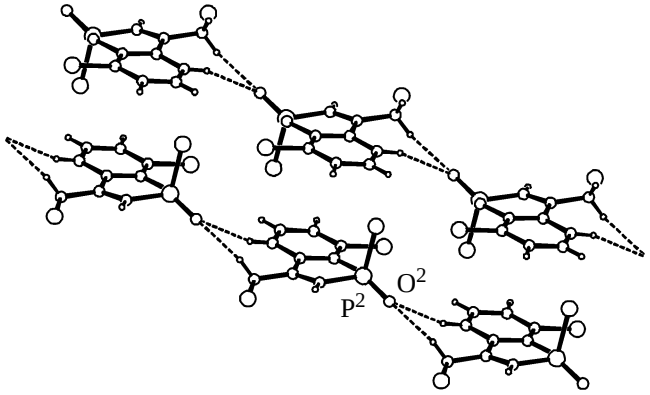


Fig. 2. Chains of hydrogen-bonded molecules of compound **III** in crystal (dashed lines).

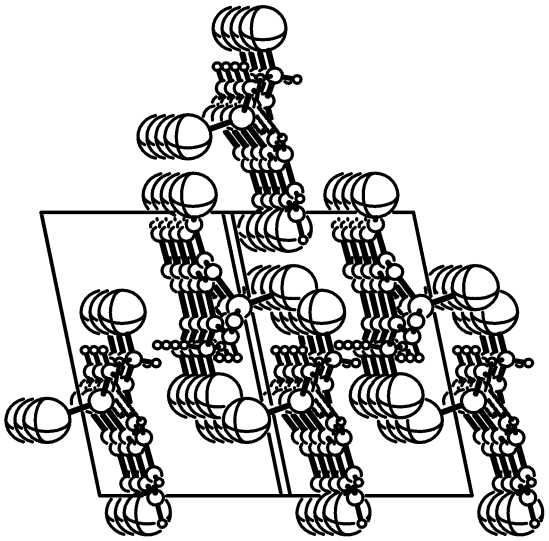


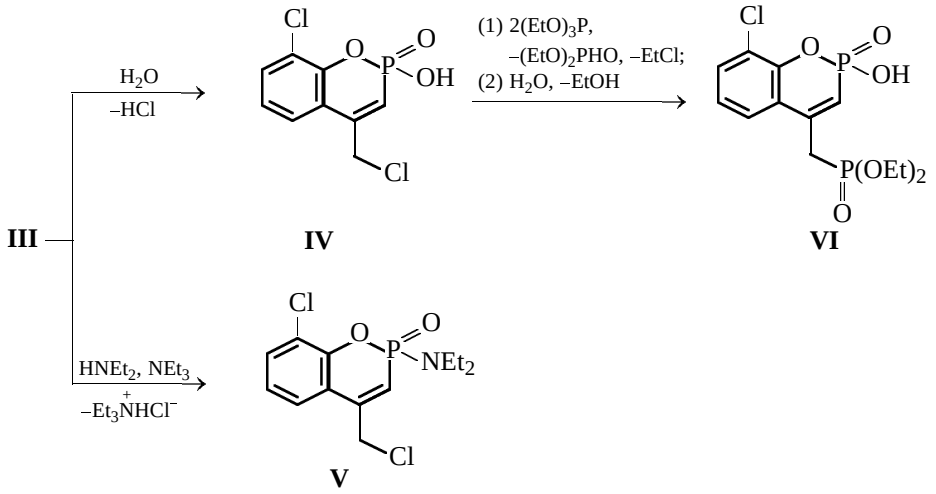
Fig. 3. Crystal packing of compound **III**. Chlorine atoms are shown by large spheres. View along the (110) crystallographic plane.

conformation favorable for interaction of the π system of the $C^3{=}C^4$ bond with the antibonding orbital of the $P^2{-}Cl^2$ bond is formed along the $P^2{-}C^2$ bond [$Cl^2P^2 \cdot C^3C^4$ dihedral angle 89.3(4)°].

The system of intermolecular hydrogen bonds in the crystal of compound **III** is mostly determined by C–H···O and π–π-type contacts. The phosphoryl O^2 atom forms a bifurcate hydrogen bond with the H^5 atom of the condensed benzene ring and the methylene H^{91} atom; as a result, chains of hydrogen-bonded molecules, running along the crystallographic direction (–110) (Fig. 2), are formed, because each molecule is involved in two such contacts as a donor and an acceptor. These contacts have the following parameters: $d(H^5\cdots O^{2'})$ 2.52(6) Å, $d(C^5\cdots O^{2'})$ 3.43(1) Å, $C^5{-}H^5\cdots O^{2'}$ angle 164(5)°; $d(C^9\cdots O^{2'})$ 3.25(1) Å, $C^9{-}H^{91}\cdots O^{2'}$ angle 148(3)° [symmetry code (–1 + *x*, 1 + *y*, *z*)]. Molecules in such chains form π-dimers with their centrosymmetric molecules in a neighboring antiparallel chain (the distance between the centers of condensed benzene rings is 3.815(2) Å, the shortest distance between the planes is 3.37 Å, and the dihedral angle is 0.0°). Hence, a supramolecular structure is formed in the crystal. In this structure, the C–H..O and π–π intermolecular interactions are realized along two mutually perpendicular directions. The crystal packing in **III** is a packing of the above-described supramolecular structures parallel to the (110) plane (Fig. 3). Therewith, the heterocyclic fragments of all molecules in the crystal are almost coplanar to this plane. It is interesting to note that such a mutual location of molecules results in localization in the crystal of fields with chlorine atoms and formation of pseudo-channels running in the same direction as the supramolecular structure. The observed multiple Cl–Cl contacts between between neighboring molecules have distances spanning the range 3.30–3.66 Å. Note that similar pseudochannels we previously observed in the crystals of 6-(alkylaminocarbonyl)-4-phenyl-1,2λ^5-benzoxaoxaphosphinin-2-one derivatives [11]. Such packing provides a fairly high packing coefficient (70.8%). According to calculations, the unit cell contains no voids potentially available for solvent molecules.

We have studied some chemical properties of phosphinine **III**. Hence, hydrolysis of compound **III** gave phosphonic acid **IV** with preserved cyclic structure. The reaction with diethylamine leads to amide **V**. The reaction of hydroxyphosphinine **IV** with triethyl phosphite proceeds in an excess of the latter to give a hydrolytically unstable 8-chloro-2-ethoxy-4-(diethoxyphosphinoylmethyl)-1,2λ^5-benzoxaphosphinin-2-one that under the isolation conditions converts into 2-hydroxy derivative **VI**. The structure of compounds **IV**–**VI** was established by means of ^{1}H, ^{13}C, and ^{31}P NMR and IR spectroscopy (see Table 1 and Experimental).

The reaction of benzophosphole **I** with propyne **II** under more rigid conditions (heating in an excess of the latter) leads to a more complex mixture of compounds, that contains, along with phosphinine **III**, three compounds. In the ^{31}P NMR spectrum, they are characterized by doublets with δ_P 17.0–19.0 ppm ($^2J_{PCH}$ 24.2–27.0 Hz). The ^{13}C–{^{1}H} and ^{13}C NMR spectra (Table 1) of the reaction mixture purified from



volatile admixtures in a vacuum allowed these compounds to be characterized as chlorinated phosphinines **III, VII**, and **VIII** and unsubstituted compound **IX**, formed in a 9:8:20:4 ratio.

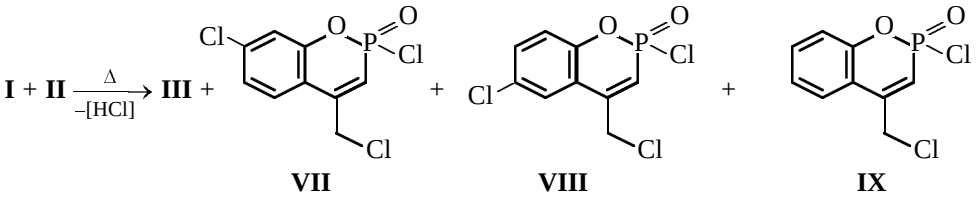


Figure 4 shows the upfield fragment of the $^{13}C–\{^1H\}$ NMR spectrum (in $CDCl_3$) of the reaction mixture of phosphole **I** and propargyl chloride, freed of volatile admixtures. All signals are sufficiently well resolved, which allows complete interpretation of the spectral data. The spectrum was interpreted with account for the multiplicities and intensities of the corresponding signals in the ^{13}C NMR spectrum, as well as spectral data for pure compound **III**. The spectral parameters show that the preferred compound formed under these conditions is 6-chloro-substituted isomer **VIII**.

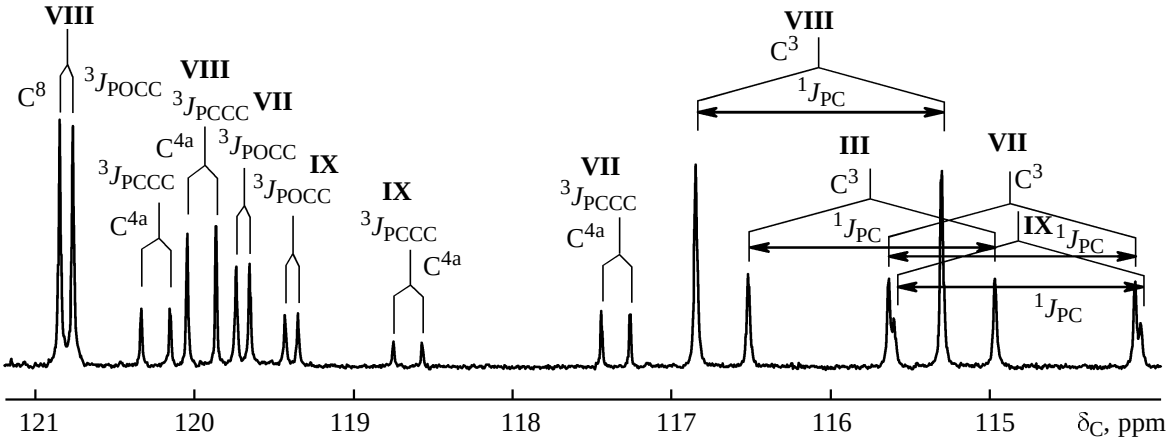
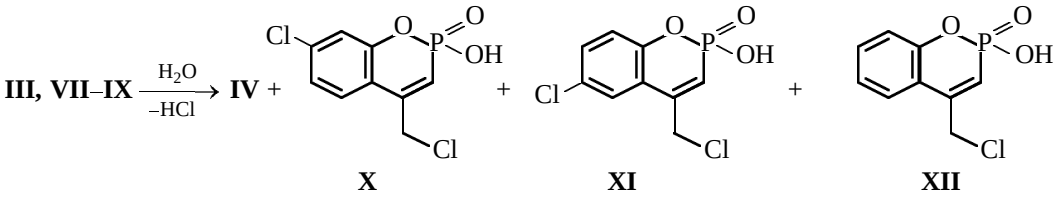


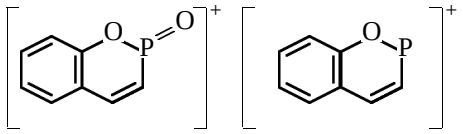
Fig. 4. Fragment of the $^{13}C–\{^1H\}$ NMR spectrum (100.6 MHz, $CDCl_3$) of the reaction mixture of phosphorane **I** with propargyl chloride, purified from volatile admixtures in a vacuum (0.1 mm Hg).

Hence, the reaction of 3-chloropropyne with benzophosphole **I**, like with arylacetylenes, provides 1,2-benzophosphinines, but chlorination of the phenylene fragment is less selective, and, depending on reaction conditions, chlorine can enter *ortho* or *para* to the endocyclic oxygen atom of the phosphinine heteroring.

Hydrolysis of the mixture of phosphinines **III** and **VII**–**IX** gave hydroxy derivatives **IV** and **X**–**XII**. By fractional crystallization we could only obtain fractions enriched with compound **XI** and containing 10–20% of phosphinine **IV**. The structure of isomer **XI** was established by means of the ^{1}H and ^{13}C NMR spectra (see Table 1 and Experimental). The structure of *meta* isomer **X** was established from a comparison of its spectral parameters with those for a pure compound obtained by the reaction of benzophosphole **I** with 3-chloropropyne in the presence of triethylbenzylammonium chloride according to [12].



The presence of chlorinated acids **IV** and **XI** in the isolated fractions was also confirmed by electron impact mass spectroscopy. The mass spectrum contains a molecular ion peak at *m/z* 264 corresponding to the formula $C_9H_7Cl_2O_3P$. Fragmentation begins with loss of a water molecule to form an *m/z* 246 ion. The peak with *m/z* 229 belongs to an $[M - Cl]^{+\cdot}$ ion. This ion also readily loses water to give an *m/z* 211 ion. The latter decomposes to form ion **A** (*m/z* 165), that gives the base peak in the mass spectrum. The peak at *m/z* 149 belongs to ion **B**. Lower *m/z* ion peaks are probably formed by consecutive decomposition of the above-mentioned ions.

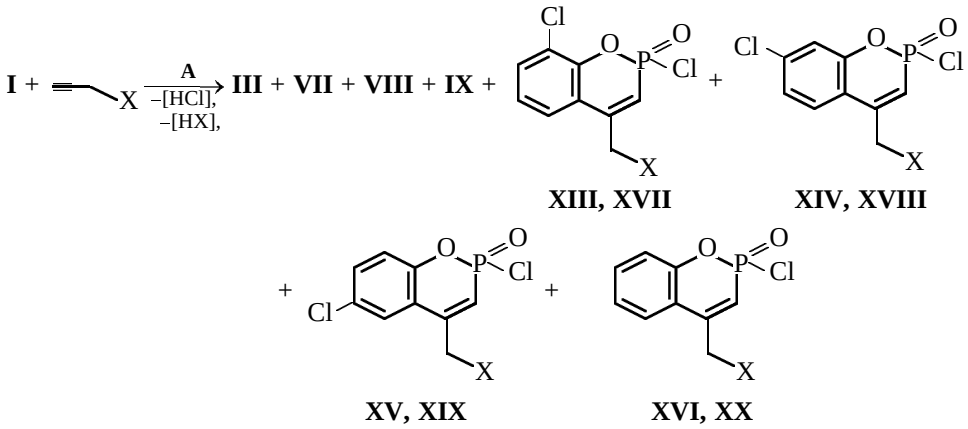


A **B**

Furthermore, the mass spectra of some of the obtained fractions of crystals containing, along with compounds **IV, X**, and **XI**, unsubstituted derivative **XII** show its moleculecular ion peak at *m/z* 230 corresponding to the composition $C_9H_8ClO_3P$.

The reactions of trichlorobenzophosphole **I** with 3-bromo- and 3-iodopropyne take an even more intricate pathway and no longer involve regioselective chlorination of the phenylene fragment. Hence, the reaction with 3-bromopropyne yields eight benzophosphinine derivatives (**III, VII**–**IX**, and **XIII**–**XVI**). Such a great number of products is explained by the side substitution of bromine with chlorine in the side chain (Finkelstein-like reaction). Changing of the reaction medium (methylene chloride or excess 3-bromopropyne) and temperature changes nothing more than the ratio of the resulting compounds. Hence, with a fourfold excess of 3-bromopropyne, the fraction of 4-bromomethyl-substituted phosphinines to 70–80%, but the chlorination of the benzo fragment occurs with almost the same regioselectivity and results in preferential formation of *ortho* and *para* isomers **III, VIII, XIII**, and **XIV**. Analysis of the ^{13}C NMR spectra of various reaction mixtures purified from volatile admixtures and high-boiling mixtures of compounds isolated by vacuum distillation, as well as comparison with the spectra of chlorinated phosphinines **III** and **VII**–**IX** allowed complete spectral identification of bromine-containing reaction products **XIII**–**XVI**. The ^{13}C NMR spectral parameters are listed in Table 1. The ^{13}C NMR spectra are well resolved. As an example, Fig. 5 shows a fragment of the upfield part of the ^{13}C–{^{1}H} NMR spectrum of a high-boiling fraction obtained by distillation of the reaction mixture of 3-bromopropyne and phosphorane **I** (the reaction was carried out at elevated temperature).

Note that the ratio of bromomethyl-containing phosphinines **XIII**–**XVI** is close to that of chlorine-containing compounds **III, VII**–**XI**. Inspite of the occurrence of bromine–chlorine exchange, we failed to detect products of bromine migration into the phenylene fragment of benzophosphinines. Evidently, the bromide ion evolving in the course of this process is completely consumed for addition, as HBr,

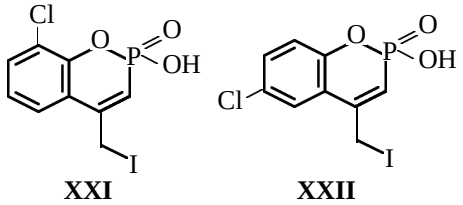


X = Br (**XIII**–**XVI**), I (**XVII**–**XX**).

Br_2, or BrCl, to excess 3-bromopropyne.This fact is confirmed by the extremely complex spectrum of volatile halogen-containing alkenes separated from phosphorus-containing reaction products by distillation. The occurrence of the side substitution of bromine with chlorine shows that halogenation precesses in the benzophosphole **I**–3-bromopropyne system are heterolytic in nature.

The same complex picture, i.e. the formation of a mixture of compounds **III, VII**–**XI**, and **XVIII**–**XX**, is observed in the reaction with 3-iodopropyne. Analysis of the NMR spectra shows that all phosphorus-containing compounds have the benzophosphinine nature (δ_P 16.0–17.0 ppm). Iodine–chlorine exchange reactions give a complex mixture of alkenes formed by addition of HCl, Cl_2, HI, J_2, and ICl to the starting 3-iodopropyne.

After hydrolysis of the reaction mixture with subsequent crystallization from aqueous acetone we could isolate a small amount of a mixture of the *ortho*- and *para*-chlorine-substituted (iodomethyl)phosphinines **XXI** and **XXII** in a 8 : 13 ratio, The composition of the compounds was confirmed by elemental analysis.



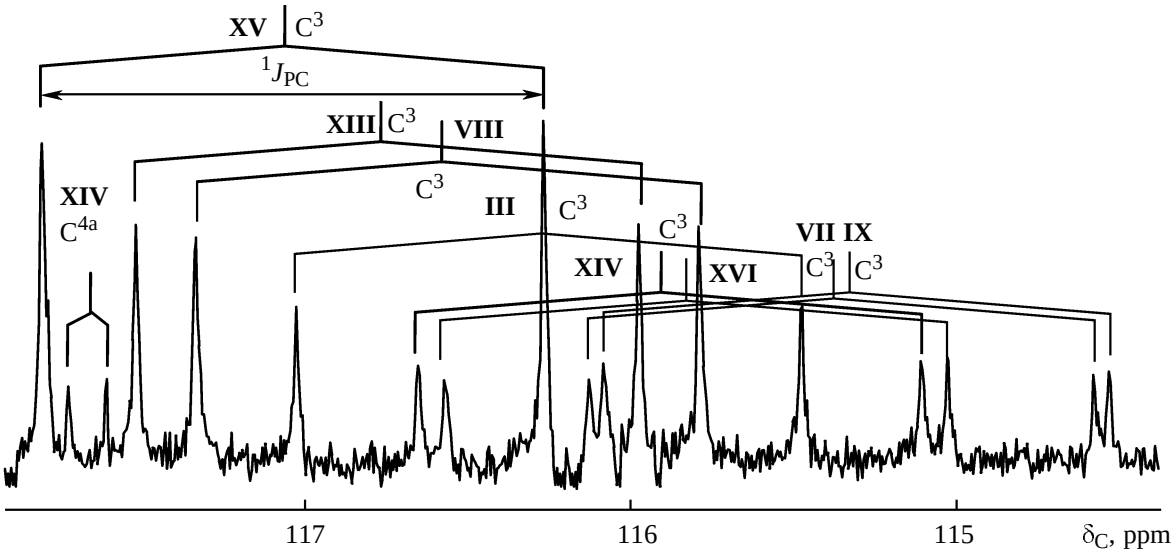
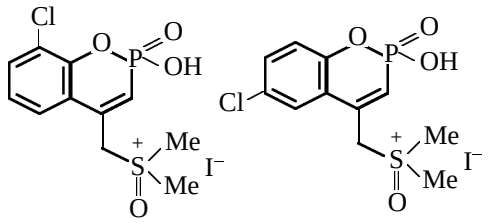


Fig. 5. Fragment of the ^{13}C NMR spectrum (100.6 MHz, $CDCl_3$) of the fraction with bp 175–180°C (0.1 mm Hg), obtained by vacuum distillation of the reaction mixture of phosphorane **I** and propargyl bromide (mixture of phosphinines **III, VII**–**IX**, and **XIII**–**XVI**).

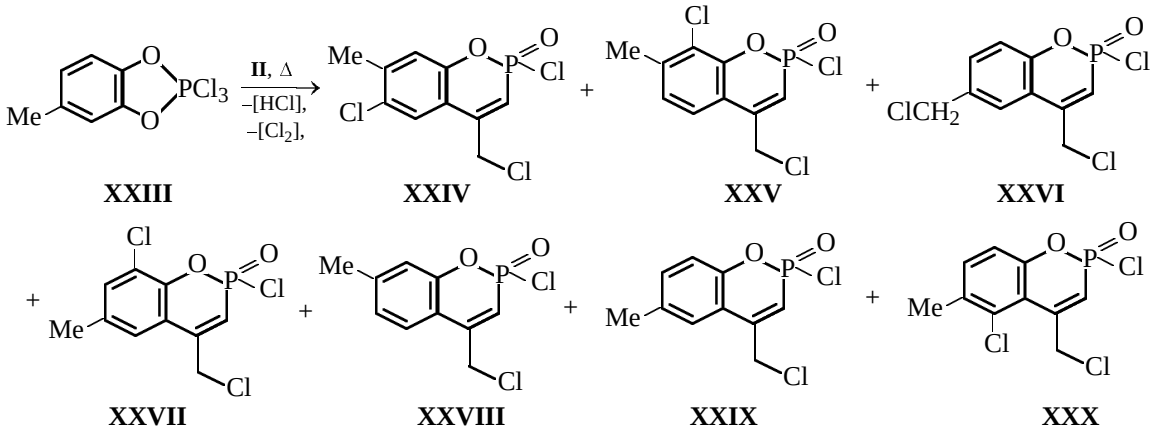
Because of the poor solubility of compounds **XXI** and **XXII** in ordinary solvents, we recorded their NMR spectra in DMSO-d_6. The ^{31}P NMR spectrum contains two closely located signals with δ_P 5.57 and 5.58 ppm ($^2J_{PCH}$ 14.2–15.8 Hz), assignable to a tetrahedral phosphorus with one P–C bond. The ^{1}H NMR spectrum (250 MHz) contains two broadened doublets with corresponding $^2J_{PCH}$ constants. In the upfield region, a broadened signal is observed at δ 2.95 ppm. It might be attributed to protons of the CH_2I group of both compounds. At the same time, the ^{13}C NMR spectrum (Table 1) contains in the upfield range a strongly broadened doublet at δ_C 31.5 ppm. Such chemical shift disagrees with published data [13] according to which the signal of the CH_2I group should appear at δ_C –2 to 10 ppm because of the effect of iodine shielding. Evidently, in our case, DMSO-d_6 is alkylated with compounds **XXl, XXII** to form salts **XXIa** and **XXIIa**. This reaction is analogous to the reversible reaction of DMSO with methyl Iodide, reported in [14].



XXIa **XXIIa**

The above chemical shift (δ_C 31.5 ppm) and other ^{1}H and ^{31}P spectral data correspond to the CH_2S surrounding. Attempted isolation of these salts was unsuccessful because of redox processes accompanied by HI and I_2 evolution. The location of the chlorine atoms in the benzo fragment was also established by means of ^{13}C NMR spectroscopy (100.6 MHz). The spectrum contains two signals of carbon atoms bound with chlorine. Their parameters [C^8, δ_C 122.80 ppm, d, $^2J_{POCC}$ 5.8 Hz (**XXIa**); C^6, δ_P 127.56 ppm, s (**XXII**)] agree with data for related compounds **III** and **VIII**.

To assess the effect of substituents in the benzo fragment of the starting phosphole on the regiochemistry of the reaction with 3-chloropropyne, we reacted the latter with methyl-substituted phosphole **XXIII**. It was found that, independent of reaction conditions (prolonged standing at 20°C or heating in excess alkyne), a mixture of five or seven benzophosphinines is formed. Two major products (total content 70–90%) crystallize from reaction mixtures in a roughly 3 : 1 ratio. Analysis of the ^{13}C NMR (Table 1), ^{1}H and ^{31}P spectra (see Experimental) shows that the major products are *para*- and *ortho*-substituted phosphinines **XXIV** and **XXV**, the *p*-chloro isomer prevailing. By means of ^{13}C NMR (Table 1) we could identify all obtained minor benzophosphinines. Figure 6 presents a fragment of the ^{13}C–{^{1}H} NMR spectrum of the high-boiling fraction containing all major and minor compounds. All signals are well resolved, and, based on the ^{13}C–{^{1}H} NMR spectra of several fractions with different phosphinine ratios and the spectra of compounds **XXIV** and **XXV**, we assigned structures **XXVI**–**XXX** to the reaction products.



XXIII **XXIV** **XXV** **XXVI**

XXVII **XXVIII** **XXIX** **XXX**

High-resolution electron impact mass spectrometry, too, provides evidence to show the benzophosphinines present in the reaction mixtures and distilled fractions comprise two or three chlorine atoms. Hence, the mass spectrum of a mixture of crystalline phosphinines **XXIV**–**XXV** shows a single *m/z* 296 peak belonging to the molecular ion $M^{+\cdot}$ of these molecules. At the same time, the mass spectrum of a mixture of

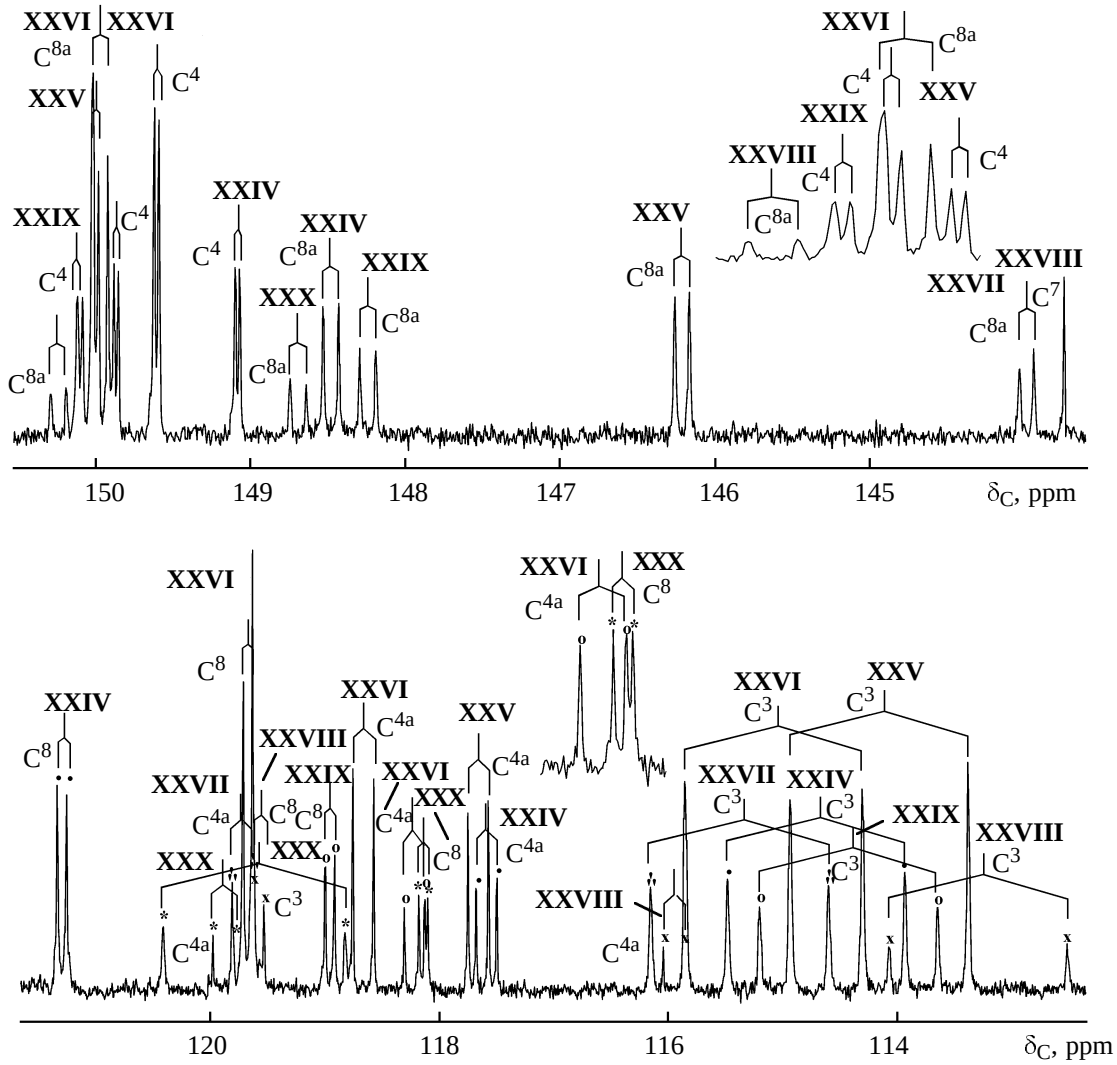
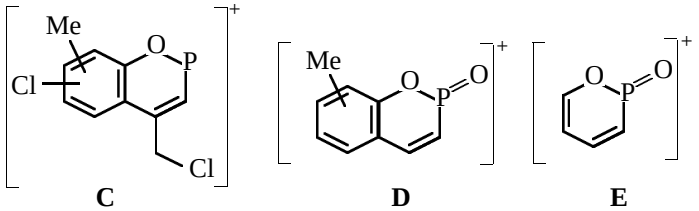


Fig. 6. (a) Downfield and (b) upfield fragments of the $^{13}C-\{^1H\}$NMR spectrum (100.6 MHz, $CDCl_3$) of the reaction mixture of phosphorane **I** with propargyl chloride after removal of volatile admixtures (mixture of compounds **XXIV**–**XXX**).

compounds **XXIV**–**XXX** shows peaks at *m/z* 296 and 262, attributed to the molecular ions $M^{+\cdot}$ of isomeric molecules containing three and two chlorine atoms, respectively. The intensity ratio of isotope $M^{+\cdot}$ peaks (*m/z* 296, 298, and 300) for phosphinines **XXIV, XXV, XXVI, XXVII,** and **XXX** is 1.0 : 0.96 : 0.32, which agrees with the empirical formulas of the compounds. For compounds **XXVIII, XXIX**, the respective *m/z* 262, 264, and 266 peak ratio is 1.0 : 0.64 : 0.12, which, too, agrees with the empirical formulas. Evidence for the presence of a mixture of compounds in the high-boiling fraction also comes from the mass spectra obtained at various injection temperatures. At the injection temperature 35°C, the intensity ratio of the M^+ peaks at *m/z* 296 and 262 is 0.93, while at 1007°C it increases to 2.0. This results points to fractionation of the sample in the course of the mass spectral experiment and its enrichment with phosphinines containing three chlorine atoms (**XXIV, XXV, XXVI, XXVII,** and **XXX**). The mass spectrum of compounds **XXIV, XXV** contains an intense peak at *m/z* 261 formed by loss of chlorine ($[M - Cl]^+$ ion). The other intense peak relates to an *m/z* 197 ion. It is evidently formed by further fragmentation of the [*M* – Cl] ion and has structure **C**. The peak at *m/z* 179 probably belongs to ion **D**. The latter ion is formed by consecutive fragmentation of the $[M - Cl]^+$. The intense peak at *m/z* 115 evidently relates to ion **E** formed on more profound fragmentation stages of the $[M - Cl]^+$ ion. The base peak at *m/z* 47 in the mass spectrum of phosphinines **XXIV, XXV** evidently relates to a $[PO]^+$ ion.



C **D** **E**

Hence, the reaction of methylbenzophosphole **XXIII** with acetylene **II**, while resulting in exclusive formation of benzophosphinine products, is characterized by a moderate regioselectivity of *ipso* substitution of oxygen (80–93% of products of substitution of oxygen in the *para* position to the methyl group). The regioselectivity of chlorination of the benzo fragment, too, is not high, but isomer **XXIV** with the chlorine atom *para* to the endocyclic oxygen atom is preferred. Two sufficiently unusual isomers **XXVI** and **XXX** are formed formed by chlorination of the methyl group and the carbon atom *ortho* to the C^4 atom of the phosphinine heteroring.

We failed to separate the mixture of phosphinines **XXIV** and **XXV** by multiple crystallization. Even the single crystal suitable for X-ray diffraction analysis was a solid solution with the same **XXIV**:**XXV** ratio of 3:1. The resulting data (selected bond lengths and bond and torsion angles) are listed in Table 3. Figure 7 shows a general view of both molecules in crystal.

As seen from the figure, the chlorine atom really resides *para* (**XXIV**) or *ortho* (**XXV**) to the endocyclic oxygen atom of the phosphinine heteroring. As the parameters of the heterorings in both molecules are equal, further discussion concerns only one of them. The heteroring contains two planar $C^4C^{4a}C^{8a}O^1$ and $P^2C^3C^4C^{4a}$ fragments (within 0.02(3) and 0.02(3) Å, respectively). The deviations of P^2 and C^3 from the $C^4C^{4a}C^{8a}O^1$ plane are 0.5612(9) and 0.240(3) Å, respectively. The O^1 and C^{8a} atoms deviate from the other planar fragment to the one side but by different distances [–0.489(2) and –0.214(3) Å,

Table 3. Selected bond angles (ω, deg), interatomic distances (*d*, Å), and torsion angles (τ, deg) in the molecules of compounds **XXIV, XXV**[a]

Bond	*d*	Bond	*d*	Bond	*d*
Cl^2–P^2	2.017(1)	P^2–O^1	1.577(2)	C^{4a}–C^{8a}	1.396(5)
Cl^8–C^8	1.473(8)	O^1–C^{8a}	1.406(4)	C^{8a}–C^8	1.368(5)
Cl^6–C^6	1.718(5)	C^3–C^4	1.350(5)	C^7–C^8	1.399(6)
Cl^9–C^9	1.775(4)	C^4–C^{4a}	1.458(4)	C^7–C^{10}	1.520(5)
P^2–O^2	1.454(4)	C^4–C^9	1.504(5)	C^6–C^7	1.381(6)
P^2–C^3	1.747(4)	C^{4a}–C^5	1.404(5)	C^5–C^6	1.378(5)
Angle	ω	Angle	ω	Angle	ω
$Cl^2P^2O^1$	102.5(1)	$P^2C^3C^4$	120.7(3)	$C^{4a}C^{8a}C^8$	124.1(3)
$Cl^2P^2O^2$	111.3(1)	$C^3C^4C^{4a}$	121.9(3)	$Cl^8C^8C^{8a}$	128.7(4)
$Cl^2P^2C^3$	106.2(1)	$C^3C^4C^9$	122.0(3)	$Cl^7C^7C^8$	111.0(4)
$O^1P^2O^2$	112.4(1)	$C^{4a}C^4C^9$	116.0(3)	$Cl^6C^6C^7$	117.7(3)
$O^1P^2C^3$	104.3(2)	$C^5C^{4a}C^{8a}$	115.2(3)	$Cl^6C^6C^5$	119.5(3)
$O^2P^2C^3$	118.7(2)	$O^1C^{8a}C^{4a}$	120.6(3)	$C^5C^6C^7$	122.8(4)
$P^2O^1C^{8a}$	122.3(2)	$O^1C^{8a}C^8$	115.2(3)	$Cl^9C^9C^4$	114.1(3)
Angle	τ	Angle	τ	Angle	τ
$Cl^2P^2O^1C^{8a}$	77.6(2)	$Cl^2P^2C^3C^4$	77.6(2)	$P^2O^1C^{8a}C^{4a}$	28.0(4)
$O^2P^2O^1C^{8a}$	162.8(2)	$O^1P^2C^3C^4$	162.8(2)	$P^2O^1C^{8a}C^8$	155.2(2)
$C^3P^2O^1C^{8a}$	33.0(3)	$O^2P^2C^3C^4$	33.0(3)	$C^3C^4C^9Cl^9$	6.0(4)

[a] Solid solution containing 70% of **XXIV** (C^6–Cl^6 bond) and 30% of **XXV** (C^8–Cl^8 bond).

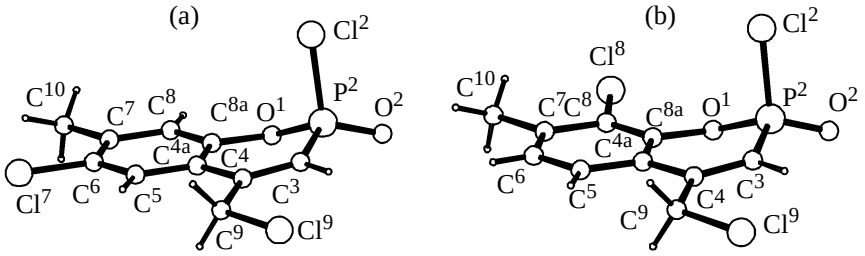


Fig. 7. Molecular geometry of compounds **XXIV** and **XXV** in crystal.

respectively]. These data show that heteroring has an unsymmetric *boat* conformation. The planar phosphinine fragments are turned about the C^4–C^{4a} bond by 9.1(5)°. Note that the $P^2C^3C^4C^{4a}C^9Cl^9$ fragment can also be considered as nearly planar (practically eclipsed conformation of the C^3–C^4 and C^9–Cl^9 bonds; $C^3C^{4a}C^{8a}O^1$ torsion angle –6.0(4)°). The phosphorus atom has a distorted tetrahedral coordination. The chlorine atom on phosphorus occupies an axial position. It deviates from the $C^4C^{4a}C^{8a}O^1$ and $P^2C^3C^4C^{4a}$ planes by 1.941(1) and 2.553(1) Å, respectively. The phosphoryl group is equatorial. The O^2 atom deviates from the $C^4C^{4a}C^{8a}O^1$ plane by 0.087(3) Å and from the $P^2C^3C^4C^{4a}$ plane by –0.722(3) Å, which is probably determined by the anomeric effect of the endocyclic oxygen atom. At the same time, the conformation along the P–C bond favors interaction of the π system of the C^3=C^4 bond with the antibonding orbital of the P^2–Cl^2 bond. The $Cl^2P^2C^3C^4$ dihedral angle is 87.9(3)°.

The presence of a methyl substituent in the condensed benzene ring of compounds **XXIV** and **XXV** leads to definite alteration in the packing of the crystal and the system of hydrogen bonds in it. In what follows we describe component **XXIV** having the highest population, even though analysis of intermolecular interactions points to insignificant alterations for the lower populated component **XXV**.

The crystal of compound **XXIV** comprises chains of molecules held together by C–H···O contacts. But, unlike compound **III**, the phosphoryl oxygen atom O^2 is only hydrogen-bonded with the methylene H^{92} proton: $d(O^2\cdots H^{92'})$ 2.39 Å, $d(O^2\cdots C^{9'})$ 3.27(1) Å, $C^{9'}$–$H^{92'}O^2$ angle 149° [symmetry code (–1 + *x*, *y*, *z*)]. The chains of molecules are located along the 0*a* crystallographic axis. Under these conditions, the methyl substituent evidently prevents molecules of such chain from approaching molecules of neighboring chains, as it was observed in compound **III**. As a result, instead of π dimers, inclined stacks of molecules are formed along the 0*c* axis. Parameters of such π–π contacts suggest weaker interactions in the stacks. The distances between the centers of the condensed rings are 4.787(2) and 4.566(2) Å, respectively, the shortest distances between the planes are 3.47 and 3.54 Å, and the dihedral angles are 0.0° (Fig. 8).

Other interactions to a greater or lesser extent fail to fit to the formal criteria for hydrogen bond: $d(D\cdots A) < R(D) + R(A) + 0.50$, $d(H\cdots A) < R(H) + R(A) - 0.12$ Å, and D–H···A angle >100.0° (D is donor and A is acceptor), accepted in the PLATON program [15]. Hence, the mutual shift of molecules leads to weakening of intermolecular π–π contacts between neighboring chains but favors formation of bulkier pseudochannels with localized chlorine atoms (Fig. 9), which is confirmed by the C–Cl distances in the crystal (3.17–3.39Å). At the same time, the methyl protons in the condensed benzene ring in **XXIV** occur to be involved in Cl···H contacts (2.87–3.14 Å).

The change of the type of substituent in the condensed benzene ring and of mutual location of molecules only slightly change the packing coefficient of **XXIV** compared to that of **III**. For the two molecular forms in the crystal of compound **XXIV**, the calculated packing coefficients are 70.2 and 69.5%. The difference in these two values shows that the chlorine substituent in the *para* position of the condensed benzene ring is slightly more favorable for crystal packing. Summarizing the crystallographic data for compounds **III** and **XXIV** we can conclude that the heterocyclic planes of molecules and pseudochannels

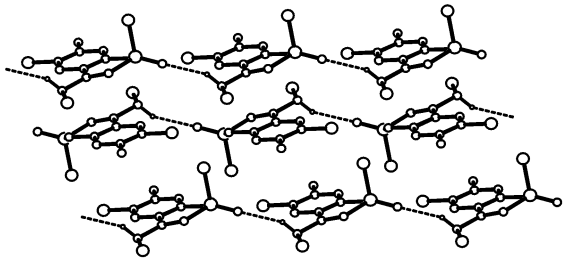
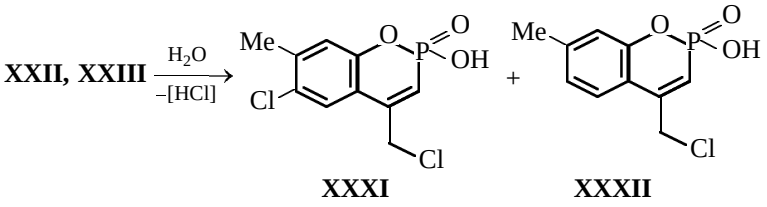


Fig. 8. System of hydrogen bonds and π–π contacts in the crystal of compound **XXIV**. Shown are only hydrogen atoms involved in hydrogen bonding.

containing chlorine atoms are oriented along selected directions. Such crystals can be suggested to possess a significant anisotropy of physical properties.

Hydrolysis of compounds **XXIV, XXV** gives phosphonic acids **XXXI, XXXII**. Their ^{13}C NMR spectra are listed in Table 1.



XXXI **XXXII**

We also studied the reaction of propargyl chloride with 5,6-dibromo-2,2,2-trichloro-1,3,2λ^5-benzodioxaphosphole **XXXIII**. The reaction proceeds under heating at 58°C for 20–25 h or at 20°C for 4 months to give a mixture of three benzophosphinines **XXXIV**–**XXXVI** in a 3 : 1 : 4 ratio. In the ^{31}P NMR spectra, they give signals at δ_P 15.2, 15.1, and 14.7 ppm. This mixture of noncrystallizing compounds freed of volatile admixtures in a vacuum was subjected to hydrolysis followed by partial crystallization, but we failed to isolate pure hydroxyphosphinines **XXXVII**–**XXXIX**. Instead two fractions of crystals were obtained. One of them contained 90% of phosphinine **XXXIX**, and the other, 90% of a mixture of compounds **XXXVII** and **XXXVIII** in a 2 : 1 ratio. These fractions were analyzed by electron impact mass spectrometry and ^1H, ^{13}C, ^{13}C–{^1H}, ^{31}P, and ^{31}P–{^1H} NMR spectroscopy (Table 1). The mass spectra of the first and second fractions show that they really are mixtures of compounds **XXXVII**–**XXXIX**. The mass spectra contain molecular ion peaks at *m/z* 386, 342, and 420. The relative intensities of isotope $M^{+\cdot}$ peaks for phosphinines **XXXVII** [386, 388, 390, 392 (1.0 : 2.3 : 1.6 : 0.32)], **XXXVIII** [342, 344, 346, 348 (1.0 : 1.6 : 0.7 : 0.1)], and **XXXIX** [420, 422, 424, 426 (1.0 : 2.6 : 2.3 : 0.83)] agree with the distributions calculated from the empirical formulas of these compounds. The ^{13}C NMR spectra provide unambiguous evidence for the the structure of the obtained hydroxyphosphinines and location of halogens in the benzo fragment.

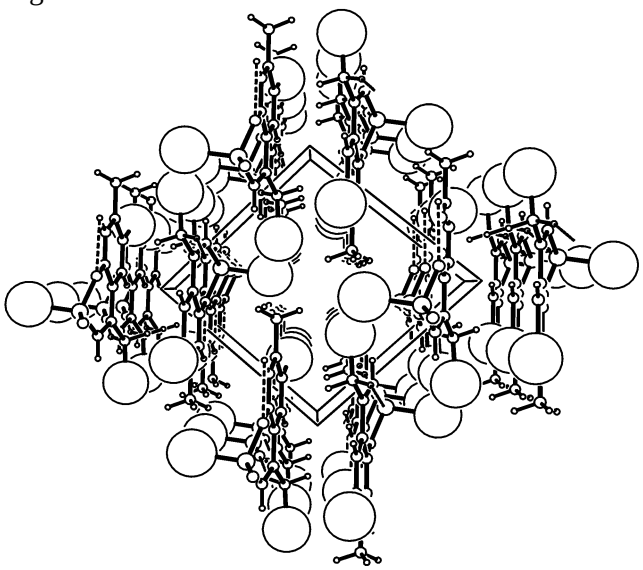
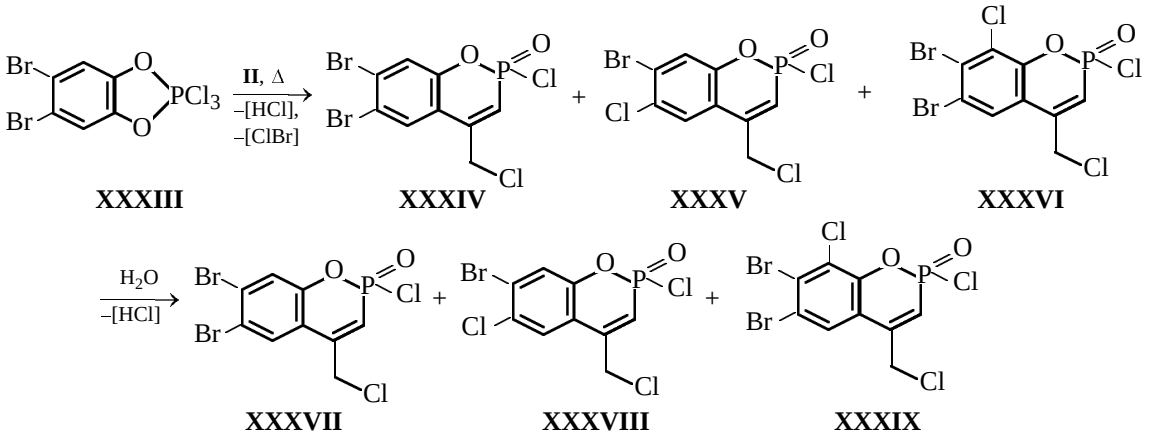


Fig. 9. Fragment of the crystal packing of compound **XXIV**. Chlorine atoms are shown by large spheres. View along the 0*a* crystallographic axis.



XXXIII **XXXIV** **XXXV** **XXXVI**

XXXVII **XXXVIII** **XXXIX**

The fact that bromine located in the 6 position of the benzophosphinine heteroring is partially substituted by chlorine follows from the presence of a characteristic signal at δ_C 122.94 ppm (C^6–Cl). The heavy atom effect makes the signal of the same carbon atom bound with bromine to shift upfield (δ_C 117.64 ppm). An unusual specific feature of this reaction is the formation of compound **XXXVI** containing chlorine in the *ortho* position to the endocyclic oxygen, which distinguish the behavior of propargyl chloride from that of arylacetylenes in the reaction with phosphorane **XXXIII** [16].

2,2,2,4,5,6,7-Heptachloro-1,3,2λ^5-benzodioxaphosphole, a phosphorane exhaustively substituted in the benzo fragment, unlike arylacetylenes, fails to react with 3-chloropropyne even under heating for 3 days at 58°C.

Hence, the reactions of 2,2,2-trichloro- and 2,2,2-trichloro-5-methyl-1,3,2λ^5-benzodioxaphospholes with 3-chloro, 3-bromo, and 3-iodopropynes occur is a much complicated fashion. The reactions all result in exclusive formation of benzophosphinines, but the regioselectivity of chlorination of the phenylene fragment is significantly lower than in the case of arylacetylenes. The effect of temperature on the reaction pathway is rather strong. Under prolonged keeping at room temperature, chlorination involves mostly the *ortho* position to the endocyclic oxygen atom of the phosphinine heteroring. Therewith, the presence of two bromine atoms in the benzo fragment of the starting phosphole does not prevent chlorine from entering into the *ortho* position to the endocyclic oxygen atom. At elevated temperatures, the *para* isomer becomes the preferred reaction product, and the regioselectivity of chlorination decreases. One more interesting peculiarity revealed itself in the reactions of trichlorobenzophosphole **I** with propargyl bromide and iodide. Along with the above-described reactions, a side reaction takes place, i.e. substitution of bromine or iodine with chlorine (Finkelstein-type reaction).

EXPERIMENTAL

The IR spectra were obtained in KBr (**IV**) or in mineral oil (**V**) on a Bruker Vector-22 Fourier spectrometer. The NMR spectra were measured on Bruker MSL-400 (400 MHz, ^{1}H; 100.6 MHz, ^{13}C, ^{13}C–{^{1}H}; 162.0 MHz, ^{31}P, ^{31}P–{^{1}H}) and Bruker WM-250 (250 MHz, ^{1}H) spectrometers against internal HMDS and external H_3PO_4. The NMR spectra were recorded in DMSO-d_6 at 40°C and in other solvents at 20°C. The mass spectra were measured on a Finnigan MAT TRACE MS spectrometer, ionizing energy 70 eV, ion source temperature 200°C. Direct sample injection into the ion source was applied. The injector ampule was heated from 35 to 150°C at a step of 35 deg min^{-1}. The mass spectra were treated using the Xcalibur program. Conditions of the X-ray diffraction analysis are presented in Table 4.

Reaction of 2,2,2-trichloro-1,3,2λ^5-benzodioxaphosphole (I) with propargyl chloride. *a*. A mixture of 8.08 g of phosphole **I** and 10 ml of propargyl chloride was kept under argon at 20°C for two months. Partial formation of a precipitate (3.08 g) was observed. It was filtered off and crystallized from methylene chloride–pentane. Analogous picture was observed in the reaction in methylene chloride (10.1 g of phosphole **I**, 6.13 g of propargyl chloride, and 20 ml of methylene chloride). 2,8-Dichloro-4-(chloromethyl)-2*H*-1,2λ^5-benzoxaphosphinin-2-one (**III**), 4.3 g (37%), was isolated, mp 159–161°C. ^{31}P NMR spectrum (162.0 MHz, C_6H_6), δ_P, ppm: 13.9 d ($^2J_{PCH}$ 24.0 Hz). The single crystal for X-ray diffraction analysis was obtained by crystallization from $CDCl_3$. Found, %: C 37.92; H 2.44; Cl 37.88; P 11.05. $C_9H_6Cl_3O_2P$. Calculated, %: C 38.09; H 2.12; Cl 37.57; P 10.93.

b. A mixture of 12.3 g of phosphole **I** and 11 ml of propargyl chloride was heated at the boiling point of the latter (58°C) for 4 h, cooled, and allowed to stand for 5–7 days. Partial precipitation of phosphinine **III** was observed. It was filtered off and crystallized from methylene chloride–pentane, yield 3.83 g (27%). ^{31}P NMR spectrum (162.0 MHz, CH_2Cl_2): 15.6 ppm, d, $^2J_{PCH}$ 24.6 Hz. The residue was washed with hexane to remove chlorinated alkenes and excess propargyl chloride and dried in a vacuum (0.1 mm Hg). The light brown glassy residue was characterized spectroscopically. ^{31}P NMR spectrum (162.0 MHz, CH_2Cl_2), δ_P, ppm: 16.02 d ($^2J_{PCH}$ 5.0–27.0 Hz, **IX**), 15.90 d ($^2J_{PCH}$ 27.5 Hz, **VII**), 15.70 d ($^2J_{PCH}$ 25.0–27.6 Hz, **VIII**), 15.62 d ($^2J_{PCH}$ 25.0–27.5 Hz, **III**). The ratio of the compounds is 4:8:20:9. The ^{13}C and ^{13}C–{^{1}H} NMR data are listed in Table 1.

8-Chloro-4-(chloromethyl)-2-hydroxy-2*H*-1,2λ^5-benzoxaphosphinin-2-one (IV) was obtained by hydrolysis of chlorophosphinine **III** in acetone–ether, yield 95%, mp 262–264°C. IR spectrum, ν, cm^{-1}: 2600–2700 v.br.s; 2300–2350 v.br.s (POH); 1606, 1561, 1440, 1465, 1480, 1403, 1350, 1280, 1268, 1240–1250, 1220, 1185, 1135, 1080, 1020, 954, 940, 925, 880, 840, 823, 794, 766, 750, 736, 730, 696, 675, 655, 625, 583, 570, 530, 505. ^{1}H NMR spectrum (250 MHz, DMSO-d_6 + CD_3CN, 1:1, 50°C), δ, ppm (*J*, Hz): 7.52 d.d (H^7, 1H, $^3J_{H^6H^7}$ 1.5); 7.47 d.d.d (H^5, 1H, $^3J_{H^6H^5}$ 8.0, $^3J_{H^7H^5}$ 1.5, $^5J_{POCCCH^5}$ 1.5); 7.13 d.d

Table 4. Parameters of crystals of compounds **III, XXIV**, and **XXV** and conditions the X-ray experiments[a]

Parameter	**III**	**XXIV, XXV**
Color, habitus	Colorless prysmatic crystals	
Syngony	Triclinic	
Space group	$P\bar{1}$	
Unit cell parameters	*a* 7241(5) Å	*a* 8.022(1) Å
	b 7.995(4) Å	*b* 9.122(2) Å
	c 10.544(5) Å	*c* 9.342(1) Å
	α 77.15(4)°	α 77.70(6)°
	β 82.76(4)°	β 66.43(6)°
	γ 63.18(5)°	γ 69.87(6)°
Volume, Å^3	534(1)	585(1)
Z	2	2
Molecular weight	283.48	297.42
d_{calc}, g cm^{-3}	1.76	1.89
Absorption coefficient, cm^{-1}	9.82	8.98
F(000)	284	300
Radiation (λ, Å)	MoK_α, λ 0.71073	
θ range	$2.12 \le \theta \le 24.7$	$2.9 \le \theta \le 22.8$
Standard reflexes	Two control by orientation and three control by intensity every 200 reflections	
Index range	$-8 \le h \le 8$	$-8 \le h \le 7$
	$-9 \le k \le 9$	$0 \le k \le 9$
	$0 \le l \le 12$	$-9 \le l \le 10$
Reflections measured	1923	1529
Number of reflections with	1019	1272
	$I > 3\sigma(I)$	$I > 2\sigma(I)$
Correction for absorption	No	No
Conditions for location and refinement of hydrogen atoms	Revealed from differential series, refined in isotropic approximation	Calculated on the basis of stereochemical criteria and refined by the rider model
Final divergence factors	*R* 0.046	*R* 0.037
	R_W 0.055	R_W 0.091
GOF parameter	2.11	1.03
Number of refined parameters	160	164
Number of unique reflections	1019	1272

[a] Enraft–Nonius CAD-4 diffractometer, ω/2θ scanning, varied scanning rate 1–16.4 deg min^{-1} by θ; corrections for intensity decay of three control reflections and for extinction were not applied; preliminary data treatment was performed using the MolEN program [17]. Both structures were solved by the direct method using the SIR program [18] and refined first isotropically and then anisotropically using the MolEN program for **III** and the SHELXL-97 [19] and WinGX programs [20] for the molecular solution of **XXIV** and **XXV**. Analysis of intermolecular contacts, including hydrogen bonds and π–π interactions in crystals, was carried out using the PLATON program [15].

(H^6, 1H, $^3J_{H^5H^6}$ = $^3J_{H^7H^6}$ 8.0); 6.50 d (PCH, 1H, $^2J_{PCH}$ 16.3); 4.61 br.s (CH_2Cl, 2H). ^{1}H NMR spectrum (400 MHz, ethanol-d_6, 23°C), δ, ppm (*J*, Hz): 7.71 d.d.d (H^7, 1H, $^3J_{H^6H^7}$ 8.0, $^4J_{H^5H^7}$ 1.5, $^5J_{POCCCH^7}$ 1.3); 7.60 d.d.t (H^5, 1H, $^3J_{H^6H^5}$ 8.0, $^4J_{H^7H^5}$ 1.5, $^5J_{HCCCCH^5}$ 1.4); 7.28 d.d.d (H^6, 1H, $^3J_{H^5H^6}$ = $^3J_{H^7H^6}$ 8.0, $^6J_{POCCCCH^6}$ 1.0); 6.66 d (PCH, 1H, $^2J_{PCH}$ 16.1); 4.82 br.s (CH_2Cl, 2H). ^{31}P–{^{1}H} NMR spectrum (162.0 MHz, DMSO), δ_P, ppm: 2.6 s. Found, %: C 40.87; H 2.78; Cl 24.64; P 12.03. $C_9H_4Cl_2O_3P$. Calculated, %: C 40.75; H 2.64; Cl 26.79; P 11.70.

8-Chloro-4-(chloromethyl)-2-(diethylamino)-2*H*-1,2λ^5-benzoxaphosphinin-2-one (V). To a solution of 2 g of chlorophosphinine **III** in 30 ml of CH_2Cl_2, a mixture of 0.6 g of diethylamine and 1 g of triethylamine was added at 20°C. The reaction mixture was left overnight and then washed with water (2 × 10 ml). The organic layer was dried over $MgSO_4$. The solvent

was removed to leave white crystals that were filtered off, washed with ether, and dried in a vacuum (12 mm). Phosphinine **V** was obtained, yield 0.35 g (40%), mp 138–139°C. IR spectrum, ν, cm^{-1}: 1598, 1555, 1435, 1360, 1296, 1280, 1245, 1210, 1186, 1160, 1120, 1098, 1080, 1039, 967, 960, 912, 860, 844, 815, 795, 755, 745, 718, 700, 653, 626, 553, 526, 503, 484. ^{1}H NMR spectrum (250 MHz, DMSO-d_6, 50°C), δ, ppm (*J*, Hz): 7.72 d.d (H^7, 1H, $^3J_{H^6H^7}$ 8.0, $^4J_{H^5H^7}$ 0.7); 7.68 d.d.d (H^5, 1H, $^3J_{H^6H^5}$ 8.0, $^4J_{H^7H^5}$ 0.7, $^4J_{POCCCH^5}$ 0.7); 7.29 d.d (H^6, 1H, $^3J_{H^5H^6} = {}^3J_{H^7H^6}$ 8.0); 6.62 d (PCH, 1H, $^2J_{PCH}$ 16.7); 4.93 m (*AB* spectrum) (CH_2Cl, 2H, $^2J_{H^AH^B}$ 12.2); 3.99 d.q ($PNCH_2$, 4H, $^3J_{PNCH}$ 12.7, $^3J_{HH}$ 7.0); 1.07 t (CH_3, 6H, $^3J_{HH}$ 7.0). Found, %: C 48.71; H 5.11; N 4.48; P 9.44. $C_{13}H_{16}Cl_2NO_2P$. Calculated, %: C 48.75; H 5.00; N 4.37; P 9.69.

8-Chloro-4-(diethoxyphosphinoylmethyl)-2-hydroxy-2*H*-1,2λ^5-benzoxaphosphinin-2-one (VI). A mixture of 0.4 g of phosphinine **III** and a threefold excess of triethyl phosphite was heated to 100–110°C. After that the reaction mixture was kept in a vacuum (0.1 mm Hg) to remove volatile admixtures. The residue was dissolved in DMSO and kept for 1 month to precipitate phosphinine **VI**, mp 142–144°C. ^{1}H NMR spectrum (250 MHz, DMSO-d_6, 40°C), δ, ppm (*J*, Hz): 7.64 d.d (H^7, 1H, $^3J_{H^6H^7}$ 8.0, $^4J_{H^5CCCH^7}$ 1.4); 7.50 br.d (H^5, 1H, $^3J_{H^6H^5}$ 8.0, $^4J_{H^7CCCH^5}$ 1.4, $^5J_{POCCCH^5}$ 0.6); 7.12 d.d (H^6, 1H, $^3J_{H^5H^6} = {}^3J_{H^7H^6}$ 8.0); 6.36 br.d.d (PCH, 1H, $^2J_{PCH}$ 15.9, $^4J_{PCCCH}$ 4.0); 3.99 d.q ($POCH_2$, 4H, $^3J_{POCH}$ 8.1, $^3J_{HH}$ 7.0); 3.34 d (CH_2P, 2H, $^2J_{PCH}$ 18.9). ^{33}P–{^{1}H} NMR spectrum (162 MHz, DMSO-d_6), δ_P, ppm (*J*, Hz): –0.2 br.d (PCH=, $^4J_{PCCCP}$ 5.0); 24.0 d (PCH_2, $^4J_{PCCCP}$ 5.0). Found, %: C 42.73; H 4.81; P 17.05. $C_{13}H_{17}ClO_6P$. Calculated, %: C 42.56; H 4.64; P 16.92.

6-Chloro-4-(chloromethyl)-2-hydroxy-2*H*-1,2λ^5-benzoxaphosphinin-2-one (XI). The light brown glassy mixture of phosphinines **III** and **VII**–**IX** (9:8:20:4), ca. 10 g, was dissolved in moist ether with a small additive of acetone (ca. 10%) and kept at 20°C. The initially formed precipitate, 0.88 g, was a 1:9 mixture of the less soluble compounds **IV** and **XI**. It was filtered off, washed with ether, and dried in a vacuum (12 mm Hg). Mass spectrum of isomers **IV, XI**, *m/z* (I_{rel}, %), ion: 264 (99.2) [$M^{+\cdot}$], 246 (19.6) [$M - H_2O$], 229 (12.9) [$M - Cl^+$, 211 (24.7) [$M - H_2O - Cl]^+$. 165 (100.0), 149 (37.9), 123 (36.0), 111 (36.6), 101 (49.8), 97 (64.2), 83 (75.6), 81 (54.4), 65 (12.6), 47 (16.1), 36 (24.0). ^{1}H NMR spectrum (250 MHz, methanol-d_4, 25°C), δ, ppm (*J*, Hz): 7.70 br.d (H^5, 1H, $^4J_{H^7H^5}$ 2.4); 7.44 d.d.d (H^7, 1H, $^3J_{H^8H^7}$ 8.6, $^4J_{H^5H^7}$ 2.4, $^5J_{POCCCH^7}$ 1.3); 7.21 br.d (H^8, 1H, $^3J_{H^7H^8}$ 8.6); 6.61 d (PCH, 1H, $^2J_{PCH}$ 16.6); 4.73 br.s (CH_2Cl, 2H). ^{31}P–{^{1}H} NMR spectrum (162.0 MHz, DMSO), δ_P, ppm: 2.4 s. Found, %: C 40.77; H 2.88; Cl 26.35; P 12.44. $C_9H_7Cl_2P_3P$. Calculated, %: C 40.75; H 2.64; Cl 26.79; P 11.70.

Reaction of 2,2,2-trichloro-1,3,2λ^5-benzodioxaphosphole (I) with 3-bromopropyne. To a suspension of 4.1 g of phosphole **I** in 2 ml of CH_2Cl_2, 4.0 g (double excess) of propargyl bromide was added. The reaction mixture was heated for 10 h at 46°C until the signal of the starting phosphorane in the ^{31}P NMR spectrum (δ_P –27.0 ppm) disappeared. The solvent was then removed, and the residue was distilled in a vacuum to give 2.05 g of a viscous liquid boiling at 180–185°C (0.1 mm Hg). It was a mixture of oxaphosphinines **III** and **VII**–**IX**, 4-(bromomethyl)-2,8-dichloro-2*H*-1,2λ^5-benzoxaphosphinin-2-one (**XIII**), 4-(bromomethyl)-2,7-dichloro-2*H*-1,2λ^5-benzoxaphosphinin-2-one (**XIV**), 4-(bromomethyl)-2,6-dichloro-2*H*-1,2λ^5-benzoxaphosphinin-2-one (**XV**), and 4-(bromomethyl)-2-chloro-2*H*-1,2λ^5-benzoxaphosphinin-2-one (**XVI**). ^{31}P NMR spectrum ($CDCl_3$) (compounds **XIII**–**XVI**): 16.1, 16.5, 16.8, 17.2 ppm.

Reaction of 2,2,2-trichloro-1,3,2λ^5-benzodioxaphosphole (I) with 3-iodopropyne. A mixture of 4.9 g of phosphole **I**, 15 ml of methylene chloride, and 8.0 g of 3-iodopropyne was kept at 20°C for 14 days. During this time the mixture acquired an intense dark color, and a precipitate (1.1 g) formed, It was filtered off and hydrolyzed in moist acetone. The precipitate obtained after these operations, a mixture of 8-chloro-2-hydroxy-4-(iodomethyl)-2*H*-1,2λ^5-benzoxaphosphinin-2-one (**XXI**) and 6-chloro-2-hydroxy-4-(iodomethyl)-2*H*-1,2λ^5-benzoxaphosphinin-2-one (**XXII**) (ca. 8:13), was filtered off, washed with ether and dried, yield 0.44 g. Methylene chloride was removed from the filtrate obtained after isolation of the first precipitate, and the residue was hydrolyzed with moist acetone to give an additional 0.21 g of a mixture of acids **XXI** and **XXII**. Found, %: C 29.89; H 2.11. $C_9H_7ClIO_3P$. Calculated, %: C 30.29; H 1.96.

Reaction of 2,2,2-trichloro-4-methyl-1,3,2λ^5-benzodioxaphosphole (XXIII) with 3-chloropropyne. *a*. A mixture of 5 g of phosphole **XXIII** and 3.5 ml of 3-chloropropyne was kept under argon in 10 ml of methylene chloride for 2 months. The reaction mixture partially crystallized while handling. The precipitate was filtered off, washed with a 2:1 mixture of cold pentane and methylene chloride, and crystallized from hexane–methylene chloride. A mixture of 2,6-dichloro-(4-chloromethyl)-7-methyl-2*H*-1,2λ^5-benzoxaphosphinin-2-one (**XXIV**) and 2,8-dichloro-(4-chloromethyl)-7-methyl-2*H*-1,2λ^5-benzoxa-

phosphinin-2-one (**XXV**) in a 3:1 ratio was isolated, yield 39%. The single crystal (3:1 solid solution) for X-ray diffraction was obtained by crystallization from $CDCl_3$. ^1H NMR spectrum (400 MHz, $CDCl_3$), δ, ppm (*J*, Hz) of compound **XXIV**: 7.51 s (H^5); 7.14 s (H^8); 6.59 br.d (PCH, $^2J_{PCH}$ 21.4); 4.55 br.s (CH_2Cl), 2.40 br.s (CH_3). ^1H NMR spectrum (400 MHz, $CDCl_3$), δ, ppm (*J*, Hz) of compound **XXV**: 7.36 d (H^5, $^3J_{HCCH}$ 8.1); 7.17 d (H^8, $^3J_{HCCH}$ 8.1); 6.60 br.d (PCH_2, $^2J_{PCH}$ 21.8); 4.57 br.s (CH_2Cl); 2.44 br. (CH_3). ^{31}P NMR spectrum δ, ppm: 16.3 (**XXIV**), 16.6 (**XXV**). Mass spectrum of a mixture of phosphinines **XXIV** and **XXV**, *m/z* (I_{rel}, %), ion (peaks of ions containing the most abundant isotopes are shown): 302 (2.4), 300 (18.7), 301 (2.4), 299 (8.0), 298 (53.1), 297 (7.7), 296 (56.0) [$M^{+\cdot}$], 261 (59.2), 197 (29.9), 179 (57.1), 115 (95.6), 47 (100.0). Both compounds were also identified by the ^{13}C and $^{13}C–\{^1H\}$ NMR spectra (Table 1). Found, %: Cl 36.01. $C_{10}H_8Cl_3O_2P$. Calculated, %: Cl 36.18. The filtrate was evaporated in a vacuum (12 mm), washed with hexane to remove chlorinated alkenes, and dried in a vacuum (0.1 mm Hg). The light brown glassy residue was a mixture of five compounds, benzophosphinines **XXIV** and **XXV**, 2-chloro-4,6-bis-(chloromethyl)-2*H*-1,2λ^5-benzoxaphosphinin-2-one (**XXVI**), 2,8-dichloro-4-(chloromethyl)-4-methyl-2*H*-1,2λ^5-benzoxaphosphinin-2-one (**XXVII**), and 2-chloro-(4-chloromethyl)-7-methyl-2*H*-1,2λ^5-benzoxaphosphinin-2-one (**XXVIII**) in a 66:70:92:84:41 ratio. The mixture was characterized by spectral methods (see also Table 1). ^{31}P NMR spectrum [162.0 MHz, CH_2Cl_2, parenthesized are the multiplicities of signals in the $^{31}P–\{^1H\}$ NMR spectrum], δ, ppm ($^2J_{PCH}$, Hz): 17.01 s (d, 21.7) **XXVIII**; 16.51 s (d, 21.7) **XXV**; 16.21 s (d, 22.5) **XXIV**; 16.16 s (d, 21.8) **XXVI**; 16.02 s (d, 21.5) **XXVII**.

b. A mixture of 10.0 g of phosphole **XXIII** and 7 ml of 3-chloropropyne was kept under argon for 5 h at 58°C. After cooling, partial precipitation was observed. The reaction mixture was diluted with 10 ml of a 3:1 mixture of hexane and methylene chloride and filtered to give 2.6 g of crystals. After 2-3 days, a new crop of crystals (2.5 g) formed. The precipitates were combined and recrystallized from hexane–methylene chloride to obtain a mixture of compounds **XXIV** and **XXV** in a 3:1 ratio, yield 44%. The filtrate was evaporated, and the residue was distilled in a vacuum to give 5.2 g of a fraction with bp 180–187°C (0.1 mm Hg), which was a mixture of seven compounds: benzophosphinines **XXIV**–**XXVIII**, 2-chloro-4-(chloromethyl)-6-methyl-2*H*-1,2λ^5-benzoxaphosphinin-2-one (**XXIX**), and 5-chloro-4-(chloromethyl)-6-methyl-2*H*-1,2λ^5-benzoxaphosphinin-2-one (**XXX**) in a 28:43:44:26:10:18:15 ratio. ^1H NMR spectrum (400 MHz, $CDCl_3$), δ, ppm (*J*, Hz) of compound **XXVIII**: 7.57 d (H^5, $^4J_{HCCCH}$ 2.1); 7.45 d.d.d (H^7, $^3J_{HCCH}$ 8.5, $^4J_{HCCCH}$ 2.1, $^5J_{POCCCH}$ 2.0); 7.25 d (H^8, $^3J_{HCCH}$ 8.5); 6.60 br.d (PCH, $^2J_{PCH}$ 21.5), 4.60 br.m ($C^6–CH_2Cl$), 4.55 br.s (CH_2Cl). ^1H NMR spectrum (400 MHz, $CDCl_3$), δ, ppm (*J*, Hz) of compound **XXX**: 6.82 br.d (PCH, $^2J_{PCH}$ 22.8), 4.926 m (A) and 4.884 (B) m (CH_2Cl, *AB* spectrum, $^2J_{H^AH^B}$ 14.6, $^4J_{H^AP}$ 1.6, $^4J_{H^BP}$ 1.3, $^4J_{H^AH^3}$ 1.1, $^4J_{H^BH^3}$ 0.5–0.6, $^6J_{H^AH^8}$ 0.5–0.6, $^6J_{H^BH^8}$ 0.5–0.6), 2.31 s (CH_3). ^{31}P NMR spectrum (162.0 MHz, $CDCl_3$, parenthesized are the multiplicities of signals in the $^{31}P–\{^1H\}$ NMR spectrum) δ_P, ppm ($^2J_{PCH}$, Hz): 17.83 s (d, 22.4) **XXVI**, 17.90 s (d. 21.6) **XXVII**, 17.99 s (d, 23.5) **XXIV**, 18.15 s (d, 22.0) **XXX**, 18.25 s (d, 21.5) **XXV**, 18.61 s (d, 22.4) **XXIX**, 18.81 s (d, 22.4) **XXVIII**.

Hydrolysis of phosphinines (XXIV, XXV). A 3:1 mixture of phosphinines **XXIV and XXV**, 3.5 g, was dissolved in moist diethyl ether and kept in air. The precipitate was filtered off, washed with ether, and dried to obtain a mixture of 6-chloro-4-(chloromethyl)-2-hydroxy-7-methyl-2*H*-1,2λ^5-benzoxaphosphinin-2-one (**XXXI**) and 8-chloro-4-(chloromethyl)-2-hydroxy-7-methyl-2*H*-1,2λ^5-benzoxaphosphinin-2-one (**XXXII**) in a 1:1 ratio, yield 96%. For ^{13}C NMR data, see Table 1.

Reaction of 5,6-dibromo-2,2,2-trichloro-1,3,2λ^5-benzodioxaphosphole with 3-chloropropyne. A mixture of 2.5 g of phosphole **XXXIII** and 1.5 ml of 3-chloropropyne was refluxed under argon for 24 h. The resulting material was hydrolyzed with caution with 0.12 ml of water (the reaction proceeds with heat evolution). Three hours later, crystal formation begun. The crystals were filtered off and washed with a little CCl_4 and ether, yield 0.2 g. The crystals were a mixture of ca. 90% of 6,7-dibromo8-chloro-4-(chloromethyl)-2-hydroxy-2*H*-1,2λ^5-benzoxaphosphinin-2-one **XXXIX**, 6% of 6,7-dibromo-4-(chloromethyl)-2-hydroxy-2*H*-1,2λ^5-benzoxaphosphinin-2-one (**XXXVII**), and 4% of 7-bromo-6-chloro-4-(chloromethyl)-2-hydroxy-2*H*-1,2λ^5-benzoxaphosphinin-2-one (**XXXVIII**). ^1H NMR spectrum (600 MHz, DMSO-d_6), δ, ppm (*J*, Hz), of compound **XXXIX**: 8.00 s (H^5), 6.77 d (PCH, $^2J_{PCH}$ 16.6), 4.87 s (CH_2Cl). ^{33}P NMR spectrum of compound **XXXIX** (162.0 MHz, acetone–DMSO, 2:1), δ_P, ppm: 2.8 d ($^2J_{PCH}$ 16.6 Hz). Additional prolonged crystallization of the filtrate (CCl_4 solution), gave 0.2 g of crystals which were a mixture of compounds **XXXVII**–**XXXIX** in 6:3:1 ratio. ^1H NMR spectrum (600 MHz, DMSO-d_6), δ, ppm (*J*, Hz) of compound **XXXVII**:

7.67 s and 7.98 s (H^5 and H^8), 6.69 d (PCH, $^2J_{PCH}$ 16.4), 4.86 s (CH_2Cl). ^{31}P NMR spectrum of compound **XXXVII** (162.0 MHz, acetone–DMSO, 2 : 1), δ_P, ppm: 3.1 d ($^3J_{PCH}$ 16.4). ^1H NMR spectrum (600 MHz, DMSO-d_6), δ, ppm (*J*, Hz) of compound **XXXVIII**: 7.68 s and 7.87 s (H^5 and H^8), 6.70 d (PCH, $^2J_{PCH}$ 16.3), 4.86 s (CH_2Cl). ^{31}P NMR spectrum of compound **XXXVIII** (162.0 MHz, acetone–DMSO-d_6, 2 : 1), δ_P, ppm: 3.2 d ($^2J_{PCH}$ 16.3 Hz).

ACKNOWLEDGMENTS

The work was financially supported by the Russian Foundation for Basic Research (project nos. 03-03-32542 and 0.5-0.3-33008) and the Program for Support of Leading Scientific Schools of the Russian Federation (project no. NSh-123.2003.01).

REFERENCES

1. Mironov, V.F., Varaksina, E.N., Shtyrlina, A.A., Musin, R.Z., and Konovalov, A.I., *Zh. Org. Khim.*, 2005, vol. 42, no. 1, p. 125.
2. Mironov, V.F., Shtyrlina, A.A., Gubaidullin, A.T., Bogdanov, A.V., Litvinov, I.A., Azancheevm N.M., Latypov, Sh.K., Musin, R.Z., and Efremov, Yu.Ya., *Izv. Akad. Nauk, Ser. Khim.*, 2004, no. 1, p. 186.
3. Mironov, V.F., Shtyrlina, A.A., Varaksina, E.N., Gubaidullin, A.T., Azancheev, N.M., Dobrynin, A.B., Litvinov, I.A., Musin, R.Z., and Konovalov, A.I., *Russ. J. Gen. Chem.*, 2004, vol. 74, no. 12, p. 1841.
4. Mironov, V.F., Azancheev, N.M., Musin, R.Z., and Konovalov, A.I., *Russ. J. Gen. Chem.*, 2005, vol. 75, no. 4, p. 541.
5. Garazd, M.M., Garazd, Ya.L., Shilin, S.V., and Khilua, V.P., *Chem. Nat. Comp.*, 2000, vol. 36, no. 5, p. 485.
6. Garazd, M.M., Garazd, Ya.L., Shilin, S.V., and Khilya, V.P., *Chem. Nat. Comp.*, 2001, vol. 37, no. 5, p. 409.
7. Flavin, M.T., Rizzo, J.D., and Khilevich, A., *J. Med. Chem.*, 1996, vol. 39, no. 6, p. 1303.
8. *Terpenoidy i kumariny: Trudy botanicheskogo instituta AN SSSR im. V.L. Komarova* (Terpenoids and Coumarines, Proc. Komarov Botanic Inst. Acad. Sci. USSR), Pigulevskii, G.V., Ed., Moscow: Nauka, 1965, Ser V: Rastit. Syr'e, no. 12, p. 198.
9. Hansch, C., Hoekman, R., Leo, A., Weininger, D., and Selassie, C.D., *Chem. Rev.*, 2002, vol. 102, no. 3, p. 783.
10. Mironov, V.F., Konovalov, A.I., Litvinov, A.I., Gubaidullin, A.T., Petrov, R.R., Shtyrlina, A.A., Zyablikova, T.A., Musin, R.Z., Azancheev, N.M., and Il'yasov, A.V., *Zh. Obshch. Khim.*, 1998, vol. 68, no. 9, p. 1482.
11. Mironov, V.F., Shtyrlina, A.A., Gubaidullin, A.T., Bogdanov, A.V., Litvinov, I.A., Azancheev, N.M., Latypov, Sh.K., Musin, R.Z., Efremov, Yu.Ya., and Konovalov, I.A., *Izv. Akad. Nauk, Ser. Khim.*, 2004, no. 1, p. 186.
12. Mironov, V.F., Shtyrlina, A.A., Konovalov, A.I., Varaksina, E.N., and Azancheev, N.M., *Izv. Akad. Nauk, Ser. Khim.*, 2001, no. 4, p. 715.
13. Breitmaier. E. and Voelter, W., *Carbon-13 NMR Spectroscopy. High-Resolution Methods and Applications in Organic Chemistry and Biochemistry*, Weinheim: VCH, 1987.
14. Durst, T., *Comprehensive Organic Chemistry*, Barton, D.H. and Ollis, W.D., Eds., Oxford: Pergamon, 1979, vol. 3. Translated under the title *Obshchaya organicheskaya khimiya*, Moscow: Khimiya, 1982, vol. 5, p. 253.
15. Spek, A.L., *Acta Crystallogr., Sect. A*, 1990, vol. 46, no. 1, p. 34.
16. Mironov, V.F., Petrov, R.R., Shtyrlina, A.A., Gubaidullin, A.T., Litvinov, I.A., Musin, R.Z., and Konovalov, I.A., *Russ. J. Gen. Chem.*, 2001, vol. 71, no. 1, p. 67.
17. Straver, L.H. and Schierbeek, A.J., *MolEN Structure Determination Sytem, Program Description*, Nonius, B.V., 1994, vol. 1.
18. Altomare, A., Cascarano, G., Giacovazzo, C.D., and Viterbo, *D., Acta Crystallogr., Sect. A*, 1991, vol. 47, p. 744.
19. Sheldrick, G.M., *SHELX-97*, Release 97-2, Göttingen: Univ. of Göttingen, 1997.
20. Farrugia, L.J., *J. Appl. Crystallogr.*, 1999, vol. 32, p. 837.