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Reaction of Trihalo(phenylenedioxy)phosphoranes with Arylacetylenes: VII.[1] Regiochemistry of Reaction 2,2,2-Tribromo-5-halobenzo[*d*]-[1,3,2λ^5]dioxaphospholes with Arylacetylenes

V. F. Mironov, N. M. Azancheev, R. Z. Musin, and A. I. Konovalov

Arbuzov Institute of Organic and Physical Chemistry, Kazan Research Center, Russian Academy of Sciences, Kazan, Tatarstan, Russia

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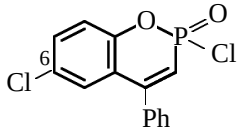
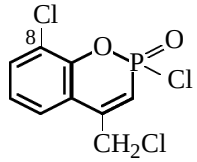
Abstract—It was for the first time shown that 2,2,2-tribromo- and 2,2-dibromo-2-fluoro-5-halobenzo[*d*]-[1,3,2λ^5]dioxaphospholes react with arylacetylenes with preferential formation of heterocycles monohalogenated in the benzo fragment, viz. 4-aryl-2-bromo(fluoro)-7-halobenzo[*e*][1,2]oxaphosphinines. Their structure was established by NMR spectroscopy. By varying in such a way the nature of the halogen at the phosphorus atom one can obtain 6- or 7-halo-substituted regioisomers of benzo[*e*][1,2]oxaphosphinines.

We recently showed that the reactions of a readily available P(V) halide, 2,2,2-trichlorobenzo[*d*][1,3,2λ^5]-dioxaphosphole (**I**), with arylacetylenes or propargyl chloride give benzo[*e*][1,2]oxaphosphinines **II** and **III**. The reactions occur in mild conditions and involve formation of a phosphorus–carbon bond and phosphoryl group, as well as *ipso*-substitution of oxygen by carbon in the benzene ring. Depending on the nature of the alkyne, chlorine is regioselectively introduced *para* (with phenylacetylene) or *ortho* (with propargyl chloride) to the oxygen atom of the phosphinine ring [2, 3].

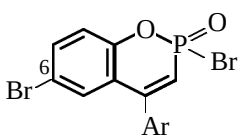


II

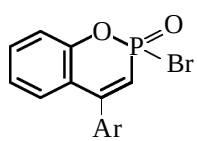


III

Unlike compound **I**, 2,2,2-tribromobenzo[*d*]-[1,3,2λ^5]dioxaphosphole (**IV**) reacts with arylacetylenes to form benzophosphinines **V** and **VI**, the latter having no bromine in the benzene ring [1].

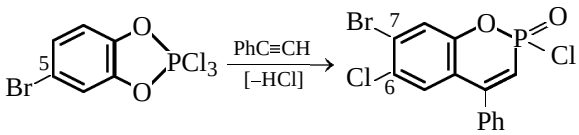


V



VI

If starting trichlorobenzophosphole **VII** contains a 5-Br substituent, chlorine is introduced in the preferentially formed benzophosphinine occurs so that both halogens are *ortho* to each other and *para* to the fused phosphinine ring [4].



VII **VIII**

In the present work we for the first time studied reactions of *P*,*P*,*P*-tribromobenzophospholes halo-substituted in the phenylene fragment (compounds **Xa** and **Xb**) with arylacetylenes. Unlike what is observed with their chlorine analogs, the bromine atom in such tribromophosphoranes is not so favorably disposed toward migration into the phenylene fragment of the benzophosphinine formed, which might allow preparation of regioisomers (with respect to the position of the halogen atom) of compounds **II** and **V**.

Phosphorane **Xa** (δ_P –188.5 ppm, CH_2Cl_2) containing chlorine in the benzene ring and obtained from derivative **IXa** reacts with phenylacetylene to form preferentially (more than 65%) a single benzophosphinine. In the ^{31}P NMR spectrum, the product gives a signal at δ_P 5.8 ppm ($^2J_{PCH}$ 27.0 Hz) and in the ^{1}H NMR spectrum (250 MHz, $CDCl_3$), a downfield doublet (δ 6.20 ppm) with the same $^2J_{PCH}$ constant. The ^{13}C NMR spectrum of the reaction mixture freed of volatile products in a vacuum, like the spectrum of

[1] For communication VI, see [1].

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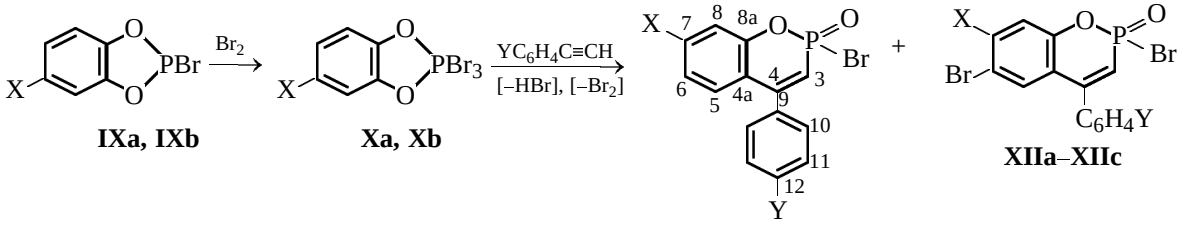
^{13}C NMR spectra (δ_C, ppm, *J*, Hz) of compounds **XIa, XIIIa, XIIIc, XIVb**, and **XVIIa**–**XIXa**

Atom	**XIa**, $CDCl_3$–CH_2Cl_2, 1 : 1	**XIIIa**,[a] ethanol-d_6–DMSO, 3 : 1
C^3	116.18 d (d.d) (141.8, PC^3; 172.1, HC^3)	114.83 d (d.d) (174.6, PC^3; 164.2, HC^3)
C^4	155.02 d (m) (2.0, PCC^4)	153.60 d (m) (2.1, PCC^4)
C^{4a}	120.01 d (m) (18.7, $PCCC^{4a}$)	121.56 d (d.d.d.d) (16.5, $PCCC^{4a}$; 7.8–8.0, $HC^6C^5C^{4a}$; 7.8–8.0, $HC^3C^4C^{4a}$; 4.9, $HC^8C^{8a}C^{4a}$)
C^5	130.56 d (br.d) (166.7, HC^5; 1.5, $POC^{8a}C^{4a}C^5$)	130.58 d (br.d) (164.0, HC^5; 1.2, $POC^{8a}C^{4a}C^5$)
C^6	125.21 d (br.d.d) (169.8, HC^6; 5.1, $HC^8C^7C^6$; 1.0, $POC^{8a}C^{4a}C^5C^6$)	124.16 d (br.d.d) (169.8, HC^6; 5.4, $HC^8C^7C^6$; 0.8, $POC^{8a}C^{4a}C^5C^6$)
C^7	137.72 s (m)	136.50 s (d.d.d) (12.0–12.1, $HC^5C^6C^7$; 4.3–4.4, HCC^7; 1.6, HCC^7)
C^8	119.88 d (d.m) (166.0, HC^8; 8.4, $POC^{8a}C^8$; 9.8, $HC^6C^7C^8$)	119.93 d (d.d.d) (168.4, HC^8; 7.5, $POC^{8a}C^8$; 4.8, $HC^6C^7C^8$)
C^{8a}	151.30 d (m) (8.4, POC^{8a})	152.64 d (d.d.d) (7.0–7.1, POC^{8a}; 9.1, $HC^5C^{4a}C^{8a}$; 4.6, HC^8C^{8a})
C^9	136.57 d (m) (20.9, $PC^3C^4C^9$)	139.07 d (d.t.d) (18.8, $PC^3C^4C^9$; 6.5, $HC^{11}C^{10}C^9$; 6.0, $HC^3C^4C^9$)
C^{10}	128.10 s (d.d) (162.6, HC^{10}; 7.2, $HCCC^{10}$; 6.9, $HCCC^{10}$)	128.79 s (br.d.d.d) (160.5, HC^{10}; 6.3, $HC^{10'}CC^{10}$; 6.2, $HC^{12}CC^{10}$)
C^{11}	128.69 s (HC^{11}; 7.1, $HC^{11'}CC^{11}$)	129.26 s (br.d.d) (160.6, HC^{11}; 6.6, $HC^{11'}CC^{11}$)
C^{12}	129.74 s (d.d) (162.0, HC^{12}; 6.7, $HC^{10}CC^{12}$)	129.59 s (d.t) (161.4, HC^{12}; 7.4–7.5, $HC^{10}CC^{12}$)

the crystalline substance isolated from this reaction mixture, contains a doublet of doublets (δ_C 116.18 ppm) with the coupling constants $^1J_{PC}$ 141.8 and $^1J_{CH}$ 172.1 Hz, whose values are close to those in compounds **V** and **VI** [2]. The spectrum contains six more signals belonging to carbon atoms directly coupled with protons, and five signals of carbon atoms not involved into such interaction. These spectral data correspond to product **XIa** which contains no bromine in the phenylene fragment. The fact that the signal of C^7 is downfield (δ 137.72 ppm) from that of C^6 (δ 130.41 ppm) [1] suggests that chlorine locates in the 7 position of benzophosphinine **XIa**. Analogously, compounds **XIb** and **XIc** are preferentially formed from 5-chlorophosphole **Xa** and *p*-tolylacetylene, as well as from 5-bromophosphole **Xb** [prepared from phosphorobromidite **IXb**] and phenylacetylene.



IXa, IXb **Xa, Xb** **XIa**–**XIc** **XIIa**–**XIIc**

X = Cl (**IXa, Xa**); Br (**IXb, Xb**); Y = H, X = Cl (**a**); Y = Me, X = Cl (**b**); Y = H, X = Br (**c**).

Compounds **XIIa**–**XIIc** in small amounts (15–20%) were detected by spectral methods. In the ^{31}P NMR spectra, they give doublets ($^2J_{PCH}$ 26.0–27.5 Hz) at δ_P 4.8 (**XIIa**) and 4.7 ppm (**XIIb, XIIc**).

Bromine and hydrogen bromide evolved in the course of the reaction add to phenylacetylene to give *cis*- *trans*-1,2-dibromo-1-phenylethenes and 1-bromo-1-phenylethene, whose spectral parameters agree with published data [2, 5].

By hydrolysis in dioxane benzophosphinines **XIa**–**XIc** and **XIIa**–**XIIc** were converted to hydroxy derivatives **XIIIa**–**XIIIc** and **XIVa**–**XIVc**, respectively. The

Table (Contd.)

Atom	**XIIIc**,[b] ethanol-d_6–DMSO, 2 : 1	**XIVb**,[c] DMSO-d_6
C^3	115.51 d (d.d) (171.8, PC^3; 164.0, HC^3)	118.15 d (d.d) (168.0, PC^3; 161.8, HC^3)
C^4	153.11 d (m) (2.0, PCC^4)	148.46 br.s (br.m)
C^{4a}	122.10 d (d.d. d.d) (16.5, $PCCC^{4a}$; 8.0, HC^6CC^{4a}; 8.0, HC^3CC^{4a}; 4.8, HC^8CC^{4a})	123.12 d (d.d. d) (16.7, $PCCC^{4a}$; 8.1, HC^3CC^{4a}; 5.7, HC^8CC^{4a})
C^5	130.75 d (br.d.d) (160.8, HC^5; 4.2, HC^6C^5; 1.2, $POCCC^5$)	131.92 s (d) (167.4, HC^5)
C^6	127.09 d (br.d.d) (170.9, HC^6; 7.3, HC^8CC^6; 0.9, $POCCCC^6$)	114.21 s (d.d) (5.1, HC^8CC^6; 3.6, HC^5C^6)
C^7	124.19 s (d.d.d) (13.5, HC^5CC^7; 4.1, HC^8C^7; 2.7, HC^6C^7)	134.02 s (d.d) (10.4, HC^5CC^7; 4.2, HC^8C^7)
C^8	122.84 d (d.d.d) (169.3, HC^8; 7.3, $POCC^8$; 5.7, HC^6CC^8; 1.3, HC^5CCC^8)	120.86 d (d.d) (170.0, HC^8; 7.0, $POCC^8$)
C^{8a}	152.66 d (d.d.d.d) (7.2, POC^{8a}; 10.0, HC^5CC^{8a}; 4.3, HC^8C^{8a}; 1.7, $HCCCC^{8a}$)	151.17 d (d.d.d) (7.2, POC^{8a}; 10.0, HC^5CC^{8a}; 4.4, HC^8C^{8a})
C^9	139.05 d (d.t.d) (18.6, $PCCC^9$; 6.5, $HC^{11}C^{10}C^9$; 6.5, $HC^3C^4C^9$)	134.82 d (m) (18.2, $PCCC^9$)
C^{10}	129.32 s (br.d.d.d) (161.7, HC^{10}; 6.7, $HC^{10'}CC^{10}$; 6.7–7.0, $HC^{12}CC^{10}$)	127.87 s (br.d.d.d) (160.5, HC^{10}; 6.0 $HC^{10'}CC^{10}$)
C^{11}	128.86 s (br.d.m) (163.3, HC^{11}; 6.9, $HC^{11'}CC^{11}$)	129.14 s (br.d.m) (160.0, HC^{11}; 5.2–5.5, $HC^{11'}CC^{11}$; 5.2–5.5, $HCCC^{11}$)
C^{12}	129.61 s (br.d.t) (161.5, HC^{12}; 7.5, $HC^{10}CC^{12}$)	138.37 s (q.t) (7.0–7.1, $HC^{10}HC^{12}$; 7.0–7.1, HCC^{12})

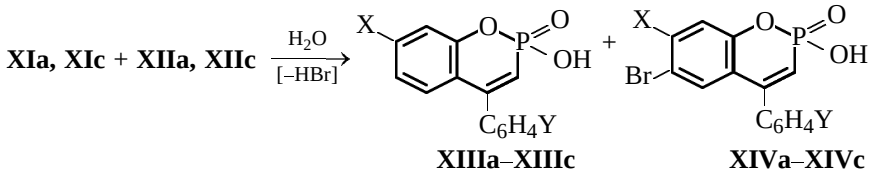
Atom	**XVIIa**, $CDCl_3$–CCl_4, 1 : 1	**XVIIIa**, $CDCl_3$–CCl_4, 1 : 1	**XIXa**,[a] $CDCl_3$–CCl_4, 1 : 1
C^3	107.62 d.d (d.d.d) (179.4, PC^3; 169.7, HC^3; 28.2, FPC)	108.80 d.d (d.d.d) (178.9, PC^3; 169.8, HC^3; 28.2, FPC)	108.97 d.d (d.d.d) (178.6, PC^3; 169.9, HC^3; 28.8, FPC)
C^4	158.80 d.d (m) (2.5, PCC^4; 2.6, FPCC)	157.74 d.d (m) (2.5, PCC^4; 2.5, FPCC)	158.42 d.d (m) (2.8, PCC^4; 3.4, FPCC)
C^{4a}	119.76 d (d.d.d.d) (17.4, $PCCC^{4a}$; 8.0, $HC^6C^5C^{4a}$; 8.1, $HC^3C^4C^{4a}$; 4.6, $HC^8C^{8a}C^{4a}$)	122.36 d (d.d.d) (17.5, $PCCC^{4a}$; 8.4, $HC^3C^4C^{4a}$; 5.3, $HC^8C^{8a}C^{4a}$)	122.36 d (m) (17.1, $PCCC^{4a}$)
C^5	130.57 d (br.d) (165.8, HC^5; 1.2, $POC^{8a}C^{4a}C5$)	133.64 d (br.d) (170.0, HC^5; 2.1, $POC^{8a}C^{4a}C^5$)	130.81 d (d.m) (1.2, $POC^{8a}C^{4a}C^5$)
C^6	124.90 s (d.d) (170.1, HC^6; 5.4, $HC^8C^7C^6$)	117.93 d (br.d.d) (8.2, $HC^8C^7C^6$; 2.1, $POC^{8a}C^{4a}C5C6$; 4.3, HCC^6)	–
C^7	137.69 s (d.d.d) (12.9, $HC^5C^6C^7$; 3.6, HC^6C^7; 3.8, HC^8C^7)	137.81 s (d.d) (10.1, $HC^5C^6C^7$; 4.6, HC^8C^7)	131.96 s (br.d.d) (169.8, HC^7; 6.9, HC^5CC^7)
C^8	119.62 d (d.d.d) (170.1, HC^8; 8.6, $POC^{8a}C^8$; 5.0, $HC^6C^7C^8$)	121.09 d (d.d) (171.1, HC^8; 8.3, $POC^{8a}C^8$)	120.74 d (d.d) (168.2, HC^8; 8.3, $POC^{8a}C^8$)
C^{8a}	151.20 d (d.d.d.d) (7.6, POC^{8a}; 9.6, $HC^5C^{4a}C^{8a}$; 5.0, HC^8C^{8a}; 1.1, $HC^3C^4C^{4a}C^{8a}$; 0, FPOC)	149.89 d (d.d.d) (7.9, POC^{8a}; 10.7, $HC^5C^{4a}C^{8a}$; 4.9, HC^8C^{8a}; 0, FPOC) 4.4, HC^8C^{8a}; 1.0, FPOC)	149.39 d.d. (d.d.d.d.d) (8.3, POC^{8a}; 10.2, $HC^5C^{4a}C^{8a}$; 8.6, $HC^7C^8C^{8a}$;
C^9	137.15 d.d (m) (18.6, $PC^3C^4C^9$; 1.1, FPCCC; 7.1, $HC^{11}C^{10}C^9$; 6.5, $HC^3C^4C^9$)	136.54 d (m) (20.4, $PC^3C^4C^9$; 7.2, $HC^{11}C^{10}C^9$; 6.5, $HC^3C^4C^9$)	136.84 d (m) (20.4, $PC^3C^4C^9$)

Table (Contd.)

Atom	**XVIIa**, $CDCl_3$–CCl_4, 1 : 1	**XVIIIa**, $CDCl_3$–CCl_4, 1 : 1	**XIXa**,[a] $CDCl_3$–CCl_4, 1 : 1
C^{10}	128.06 s (br.d.m) (161.6–162.5, HC^{10}; 5.6–6.0, $HC^{10'}$ CC^{10}; 5.6–6.0, $HC^{12}CC^{10}$)	127.97 s (br.d.m) (162.3, HC^{10}; 5.6–6.0, $HC^{10'}CC^{10}$; 5.6–6.0, $HC^{12}CC^{10}$)	128.03 s
C^{11}	128.90 s (br.d. m) (162.5, HC^{11}; 6.3, $H^{11'}CC^{11}$)	129.01 s (br.d.m) (162.5, HC^{11}; 6.3, $H^{11'}CC^{11}$)	128.89 s
C^{12}	129.82 s (d.t) (162.0, HC^{12}; 7.6, $HC^{10}CC^{12}$)	130.13 s (d.t) (162.1, HC^{12}; 7.6, $HC^{10}CC^{12}$)	129.92 s

[a] 67.31 s (t.t.t) [CH_2O (dioxane), $^1J_{HC}$ 142.7, $^3J_{HCOC}$ 2.1–2.2, $^2J_{HCC}$ 2.1–2.2]. [b] 67.09 s (t.t.t) [CH_2O (dioxane), $^1J_{CH}$ 142.6, $^3J_{HCOC}$ 2.1]. [c] 20.51 s (q.t) (CH_3, $^1J_{HC}$ 126.6, $^3J_{HCCC}$ 4.2).

^{31}P NMR signal of these compounds appears slightly upfield (3.0–3.5 ppm). The structure of the isolated major products **XIIIa** and **XIIIc** is confirmed by their ^{13}C NMR spectra (see the table). Hence, the chemical shifts of the C^5 (d.d.d.d), C^6 (d.d.d), C^7 (d.d.d), and C^{10} (br.d) signals and the coupling constants with protons and phosphorus are fully consistent with the cyclic structure of compounds **XIIIa** and **XIIIc**, as well as the *meta* position of chlorine (bromine) with respect to the phosphinine oxygen atom.



X, Y = Cl, H (**a**); Cl, Me (**b**), Br, H (**c**).

We failed to isolate minor products **XIVa** and **XIVc** pure but could obtain enriched fractions by fractional crystallization. Parameters of the ^{13}C NMR spectra of compounds **XIVa** and **XIVc** agree with those reported in [5]. Unlike phenyl derivatives **XIVa** and **XIVc**, the minor isomer **XIVb** prepared from *p*-tolylacetylene was isolated pure by crystallization from dioxane. Its structure was established by means of ^{13}C NMR spectroscopy (see table). The spectrum contains seven carbon signals not split by direct C–H spin–spin coupling and four signals that show such splitting. Such spectral pattern and the fairly upfield location of the C^6 signal (114.22 ppm), associated with shielding from the *ipso*-bromine and *para*-oxygen atoms, completely agree with structure **XIVb**.

Unlike tribromophospholes **Xa** and **Xb**, 2,2-dibromo-5-chloro-2-fluorobenzo[*d*][1,3,2]dioxaphosphole (**XVI**) prepared from P(III) derivative **XV** reacts with phenyl- and *p*-tolylacetylene in a more complicated manner to give three benzophosphinines are formed, whose ratio slightly varies, depending on the concentration of the starting reagents. In any case, one of the products is preferred (53–60%). Its fraction increases when the reaction is carried out in a more dilute solution. In the ^{31}P NMR spectrum, the products (reaction with phenylacetylene, synthesis in a "concentrated" solution) are characterized by doublets of doublets with δ_{P^1} 4.1 (53%, $^1J_{PF}$ 1065.4, $^2J_P4dC_H$ 19.3), δ_{P^2} 3.7 (24%, $^1J_{PF}$ 1064.8, $^2J_{PCH}$ 19.1), and δ_{P^3} 3.2 ppm (24%, $^1J_{PF}$ 1067.7, $^2J_{PCH}$ 18.7 Hz). Analogous doublets are present in the ^1H NMR spectrum (250 MHz): δ_1 6.14 ($^2J_{PCH}$ 19.5), δ_2 6.18 ($^2J_{PCH}$ 19.0), and δ_3 6.19 ppm ($^2J_{PCH}$ 18.8 Hz). Since we failed to isolate any of these compounds pure, the reaction mixture freed of volatile products in a vacuum (0.05 mm Hg) was investigated by mass spectrometry and ^{13}C NMR spectroscopy. The electron impact mass spectra contain only two peaks at *m/z* 372 and 294, assigned to the molecular ions $[M_1]^{+\cdot}$ and $[M_2]^{+\cdot}$ The exact masses of these ions (given are ions containing the most abundant isotopes) are 371.9230 and 293.9931, which is nicely consistent with those cal0 culated from the elemental compositions $C_{14}H_8BrCl \cdot FO_2P$ and $C_{14}H_9ClFO_2P$: 371.9118 (M_1) and 294.0012 (M_2), respectively. Considering the ^{13}C NMR spectral

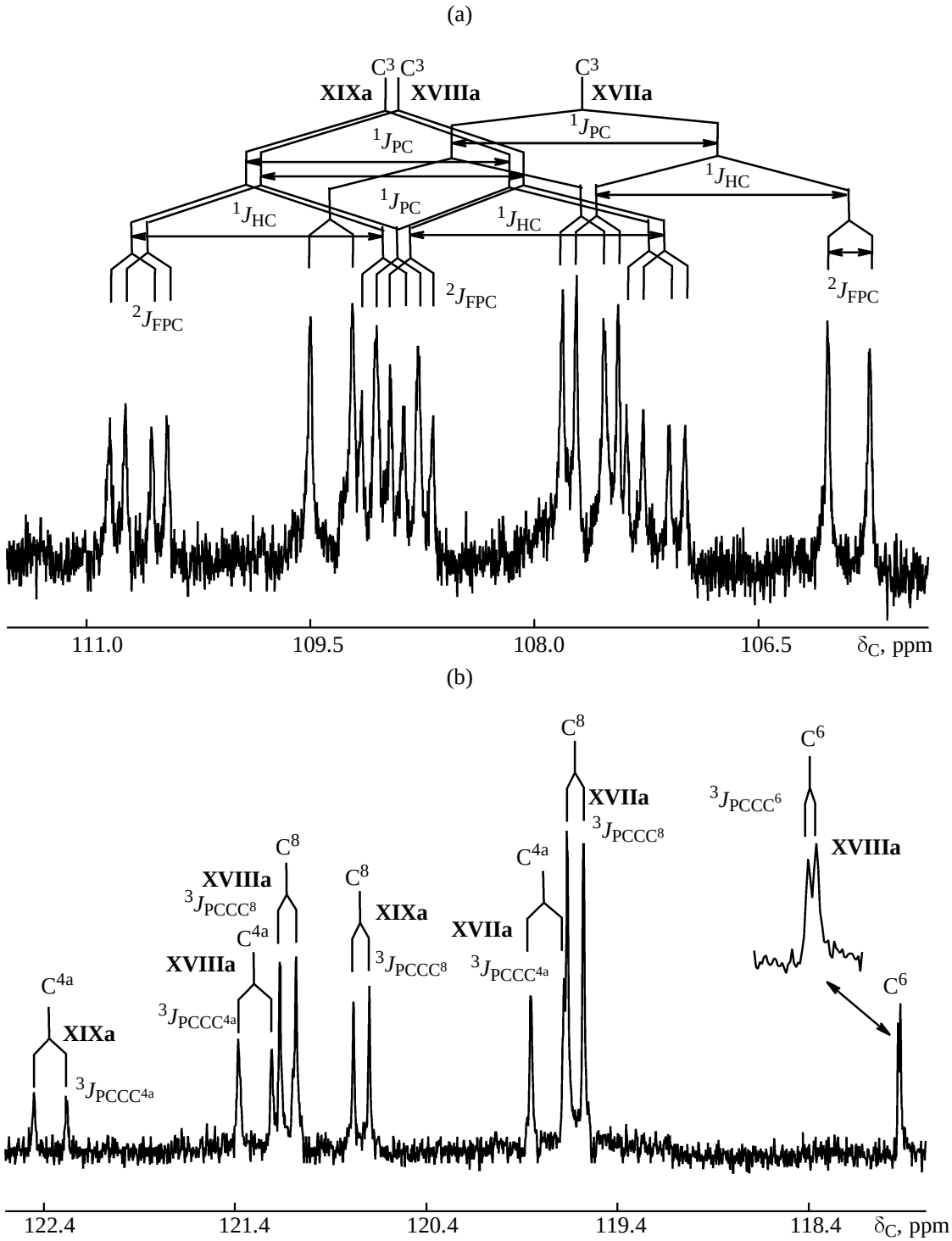
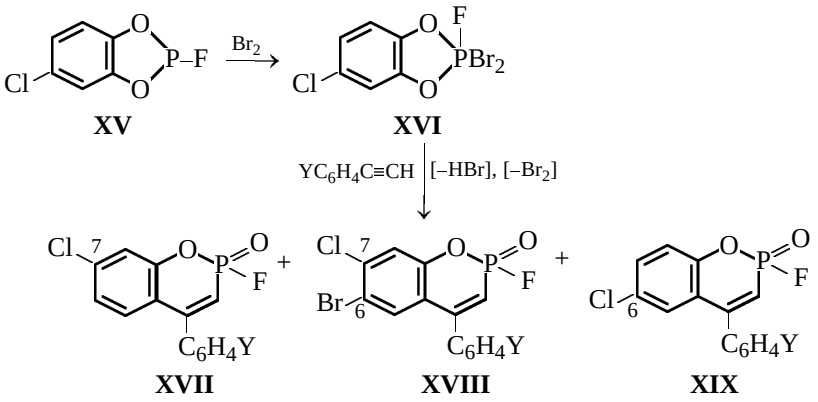


Fig. 1. Upfield regions of the (a) ^{13}C and (b) ^{13}C–{^{1}H} NMR spectra of the mixture of compounds **XVIIa**–**XIXa**.

data (see table), we assigned to the resulting compounds the structures of benzophosphinines **XVIIa**–**XIXa** (chemical shifts δ_{P^1}–δ_{P^3}, respectively). Figures 1a and 1b show the upfield regions of the ^{12}C and $^{13}C\{^{1}H\}$ NMR spectra of the mixture of compounds **XVIIa**–**XIXa**. The signals are fairly well resolved, which allows the spectra to be assigned completely. The major product **XVIIa** contains no other substituents in the phenylene fragment than 7-Cl, which is easy to establish from the chemical shift of the C^7 signal (δ_C 137.69 ppm) and its muliplicity (d.d.d, $^3J_{HC^5CC^7}$ 12.9, $^2J_{HC^6C^7} = {}^2J_{HC^8C^7}$ 3.6–3.8 Hz). The

multiplicity of the C^7 signal of compound **XVIIIa** (δ_C 137.81 ppm, d.d, $^3J_{H^5CC^7}$ 10.1 Hz, $^2J_{HC^8C^7}$ 4.6 Hz) agrees with the presence of bromine in the 6 position. The C^6 signal appears upfield from the C^7 signal (δ_C 117.93 ppm). The presence of fluorine on phosphorus in compounds **XVIIa**–**XIXa** can also be inferred from the shape of the C^4 signal (δ_C 157.74–158.8 ppm, d. d, $^2J_{FCC}$ 2.5–3.4 Hz, $^3J_{PCC}$ 2.5 Hz).

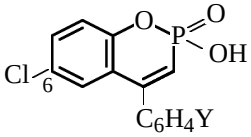


XV **XVI** **XVII** **XVIII** **XIX**

Y = H (**a**), Me (**b**).

Other parameters of the ^{13}C NMR spectrum of compound **XIXa** (see table) are much alike those of compound **II** [2].

Hydrolysis of the mixture of fluorophosphinanes **XVIIa**–**XIXa** gave hydroxy derivatives **XIIIa** and **XIIIb, XIVa** and **XIVb,** and **XXa** and **XXb**, respectively.



XXa, XXb

Y = H (**a**), Me (**b**).

By fractional crystallization we could only isolate a small amount of phosphinane **XIVb**, as well as a mixture of compounds **XIII** (most abundant), **XIV,** and **XX**. The spectral parameters of 6-chloro-substituted hydroxyphosphinines **XXa** and **XXb** are similar to those of the pure compounds prepared previously [2].

Hence, the possibility of the preferential formation of regioisomers of benzo[*e*][1,2]oxaphosphinanes containing the chlorine atom *para* to the heteroring carbon atom, via the use of tribromophosphoranes like **X** and **XVI** that already have a halogen atom in the benzene ring, has been demonstrated for the first time This synthetic result is based, on the one side, on the weaker ability of the bromide anion, compared to chloride, to migrate into the benzo fragment of the benzophosphinine system in the course of reaction of *P*,*P*,*P*-tribromo- and *P*,*P*,*P*-trichlorobenzo[*d*][1,3,2]-dioxaphospholes with arylacetylenes and, on the other, on selective *ipso* substitution of the oxygen atom located *para* to the halogen atom that is already present in the benzo fragment of the starting phosphole.

EXPERIMENTAL

The IR spectra were measured on a Specord M-80 spectrometer for suspensions in mineral oil between KBr plates. The NMR spectra were recorded on Bruker MSL-400 (^{13}C, 100.6; ^{31}P 162.0 MHz) and Bruker WM-250 (^1H, 250 MHz) spectrometers in $CDCl_3$ or ethanol-d_6 solutions at 20°C and in DMSO-d_6 solutions at 45°C. The mass spectrum was obtained on an MX-1310 instrument (ionizing energy 70 eV, collector current 30 μA) with direct inlet (*T* 120°C). The exact masses were measured automatically by the reference peaks of perfluorokerosene.

2-Bromo-5-chlorobenzo[*d*][1,3,2]dioxaphosphole (IXa). A mixture of 23.6 g of 4-chloropyrocatechol, 31.1 ml of PBr_3, and 3-5 drops of water was heated with strirring (90–110°C) for 40 min and then fractionated. Yield of dioxaphosphole **IXa** 89%, bp 82–84°C (0.1 mm Hg). $^{31}P–\{^1H\}$ NMR spectrum: δ_P 177.6 ppm.

2,5-Dibromobenzo[*d*][1,3,2]dioxaphosphole (IXb) was obtained analogously from 11.86 g of

4-bromopyrocatechol, 6.4 ml of PBr_3, and 3–5 drops of water. Yield 91%, bp 92–94°C (0.1 mm Hg). ^{31}P–$\{^1H\}$ NMR spectrum (CH_2Cl_2): δ_P 178 ppm.

5-Chloro-2-fluorobenzo[*d*][1,3,2]dioxaphosphole (XV) was prepared by fluorination of 5-chloro-2-fluorobenzo[*d*][1,3,2]dioxaphosphole [3] (15.2 g) with 18 g of antimony trifluoride. Yield 61%, bp 72–75°C (15 mm). ^{31}P–$\{^1H\}$ NMR spectrum (CH_2Cl_2), δ_P, ppm: 125.4 d ($^1J_{PF}$ 1313.7 Hz).

Reaction of 2,2,2-tribromo-5-chlorobenzo[*d*]-[1,3,2λ^5]dioxaphosphole (Xa) with phenylacetylene. Phenylacetylene, 6.1 ml, was added at 0–10°C under vigorous bubbling of argon to 12.06 g of phosphorane **Xa** (δ_P –188.5 ppm, CH_2Cl_2) prepared from 7.39 g of dioxaphosphole **IXa** and 1.57 ml of bromine in 25 ml of CH_2Cl_2 (–10 to –3°C), and the resulting mixture was kept at 20°C for 8 h. **2-Bromo-7-chloro-4-phenylbenzo[*e*][1,2λ^5]oxaphosphinine 2-oxide (XIa)** (~0.6 g) precipitated and was filtered off under argon, washed with cold CH_2Cl_2 and dried. mp 174–175°C. ^{31}P–$\{^1H\}$ NMR spectrum (CH_2Cl_2), δ_P, ppm: 5.8 d ($^2J_{PCH}$ 27.0 Hz). The filtrate was evaporated in a vacuum (first at 12 and then 0.1 mm Hg). The glassy residue and the crystals were dissolved in 20 ml of dioxane, and 0.6 ml of water was added. After 5–10 days, **7-chloro-4-phenylbenzo[*e*][1,2λ^5]oxaphosphinin-2-ol 2-oxide (XIIIa**) precipitated as white crystals (adduct with dioxane), yield 2.2 g, mp 198–201°C. IR spectrum, ν, cm^{-1}: 3056, 2540–2550 v.br, 2230–2290 v.br, 1625–1627, 1592, 1576, 1549, 1485, 1435, 1400, 1337, 1248, 1219, 1182 sh., 1078, 1020, 964, 930, 885, 860, 825, 758, 743, 725, 714, 699, 670, 651, 610, 578, 565, 542, 510, 474, 439, 412. ^{31}P NMR spectrum (DMSO), δ_P, ppm: 3.5 d ($^2J_{PCH}$ 17.5 Hz). Found, %: C 56.97; H 4.24; P 9.19; Cl 10.61. $C_{14}H_{10}ClO_3P \cdot 1/2C_4H_8O$. Calculated, %: C 57.05; H 4.16; P 9.21; Cl 10.55. Additional crystallization gave an additional 2.1 g of the dioxane adduct of phosphinine **XIIIa**.

Reaction of dioxaphosphole Xa with *p*-tolylacetylene. *p*-Tolylacetylene, 9.5 g, was added at 0–10°C under vigorous bubbling of argon to 16.48 g of phosphorane **Xa** prepared from 10.1 g of phosphole **IXa** and 2.0 g of bromine in 50 ml of CH_2Cl_2 (–10 to –3$oC). The solvent, dibromostyrenes, and excess acetylene were removed from the reaction mixture in a vacuum first at 12 and then 0.1 mm Hg. The glassy residue, a 7:1 mixture of **2-bromo-7-chloro-4-*p*-tolylbenzo[*e*][1,2λ^5]oxaphosphinine 2-oxide** (**XIb**) and **2,6-dibromo-7-chloro-4-*p*-tolylbenzo[*e*][1,2λ^5]-oxaphosphinine 2-oxide** (**XIIb**), was characterized by spectral methods. ^{31}P–$\{^1H\}$ NMR spectrum, δ_P, ppm: 6.0 d ($^2J_{PCH}$ 26.4 Hz) (**XIb**), 4.7 d ($^2J_{PCH}$ 26.3 Hz) (**XIIb**. This material was dissolved in 25 ml of dioxane, and 1.0 ml of H_2O was added. After 5–7 days, a little (0.11 g) **6-bromo-7-chloro4-*p*-tolylbenzo[*e*][1,2λ^5]oxaphosphinin-2-ol 2-oxide** (**XIV**) precipitated as white crystals, mp > 300°C. ^1H NMR spectrum (400 MHz, DMSO-d_6), δ, ppm (*J*, Hz): 7.58 s (H^5), 7.26 m and 7.33 m (C_6H_4, *AA'XX'* spectrum, $^3J_{AX} = {}^3J_{A'X'}$ 8.1), 7.31 s (H^8), 6.29 d (PCH, $^2J_{PCH}$ 17.3), 2.40 s (CH_3). ^{31}P NMR spectrum (DMSO-d_6), δ_P, ppm: 3.7 d ($^2J_{PCH}$ 17.4 Hz). Found, %: C 46.63; H 3.07. $C_{15}H_{11}BrClO_3P$. Calculated, %: C 46.69; H H 2.85. Prolonged crystallization of the mother liquor (more than a month) gave 2.21 g of a 10:1 mixture of **7-chloro-4-*p*-tolylbenzo[*e*][1,2λ^5]-oxaphosphinin-2-ol 2-oxide** (**XIIIb**) and compound **XIVb**. ^1H NMR spectrum (400 MHz, DMSO-d_6), δ, ppm (*J*, Hz) of compound **XIIIb**: 7.38 d.d (H^8, $^4J_{H^6CCCH^8}$ 2.2, $^4J_{POCCH^8}$ 1.5), 7.25 m and 7.31 m (C_6H_4, *AA'XX'* spectrum, $^3J_{AX} = {}^3J_{A'X'}$ 8.1), 7.20 d.d (H^6, $^3J_{H^5CCH^6}$ 8.5, $^4J_{H^8CCCH^6}$ 2.2), 7.12 d (H^5, $^3J_{H^6CCH^5}$ 8.5), 6.23 d (PCH, $^2J_{PCH}$ 17.8), 2.39 s (CH_3). ^{31}P NMR spectrum (DMSO-d_6) of compound **XIIIb**, δ_P, ppm: 4.7 d ($^2J_{PCH}$ 18.0 Hz).

Reaction of 2,2,2,5-tetrabromobenzo[*d*][1,3,2λ^5]-dioxaphosphole (Xb) with phenylacetylene. Phenylacetylene, 8.73 ml, was added at 0–10°C under vigorous bubbling of argon to 18.23 g of phosphorane **Xb** (δ_P –189.2 ppm, CH_2Cl_2) prepared from 11.86 dioxaphosphole **IXb** and 2.02 ml of bromine in 40 ml of CH_2Cl_2 (–10 to –3°C). The solvent, dibromostyrenes, and excess acetylene were removed from the reaction mixture in a vacuum first at 12 and then 0.1 mm Hg. The glassy residue, a 8:3 mixture of **2,7-dibromo-4-phenylbenzo[*e*][1,2λ^5]oxaphosphinine 2-oxide** (**XIc**) and **2,6,7-dibromo-4-phenylbenzo[*e*][1,2λ^5]oxaphosphinine 2-oxide** (**XIIc**), was characterized by spectral methods. ^1H NMR spectrum (250 MHz, $CDCl_3$) of compound **XIc**, δ, ppm (*J*, Hz): 6.26 d (PCH, $^2J_{PCH}$ 25.6). ^{31}P–$\{^1H\}$ NMR spectrum (CH_2Cl_2), δ_P, ppm: 3.8 d ($^2J_{PCH}$ 25.0 Hz) (**XIc**, 6.47 d ($^2J_{PCH}$ 25.6 Hz) (**XII**. This material was dissolved in 20 ml of dioxane, and 1.0 ml of H_2O was added. After 9–12 days, **7-bromo-4-phenylbenzo[*e*][1,2λ^5]oxaphosphinin-2-ol 2-oxide** (**XIIIc**) precipitated as white crystals (adduct with dioxane), yield 2.2 g, mp 220–222°C. IR spectrum, ν, cm^{-1}: 2670 v.br, 2530–2560 v.br, 2250–2300 v.br, 2150 v.br, 2150 v.br, 1643, 1590, 1576, 1545, 1400, 1340, 1250–1260, 1210, 1195, 1182, 1160, 1125, 1087, 1082, 1015, 1002, 964, 930, 895, 875, 865, 830, 768, 744, 725, 715, 700, 667, 644, 618, 575, 565, 525, 510, 475, 440. ^1H NMR spectrum (300 MHz, ethanol-d_6), δ, ppm (*J*, Hz): 7.48 m and 7.34 m (C_6H_5), 7.38 d (H^8, $^4J_{H^6CCCH^8}$ 2.0), 7.25 d.d (H^6, $^4J_{H^6CCCH^8}$ 2.0, $^3J_{H^5CCH^6}$ 8.5), 7.06 d (H^5,

$^3J_{H^6CCH^5}$ 8.5), 6.16 d (PCH, $^2J_{PCH}$ 17.9). ^{31}P NMR spectrum (DMF), δ_P, ppm: 3.6 d ($^2J_{PCH}$ 17.8 Hz). Found, %: C 50.07; H 3.48; P 7.92; Br 21.51. $C_{14}H_{10}BrO_3P \cdot 1/2C_4H_8O_2$. Calculated, %: C 50.39; H 3.67; P 8.14; Br 21.0. The mother liquor was evaporated by half to obtain an additional 2.2 g of the dioxane adduct of phosphinine **XIIIc**.

Reaction of 2,2-dibromo-5-chloro-2-fluorobenzo[*d*][1,3,2λ^5]dioxaphosphole (XVI) with phenylacetylene. Phenylacetylene, 16.49 ml, was added at 0–10°C under vigorous bubbling of argon to 26.22 g of phosphorane **XVI** prepared from 14.32 g of dioxaphosphole **XV** and 3.8 ml of bromine in 25 ml of CH_2Cl_2 (–20 to –10°C). The reaction mixture was consecutively evaporated at 12 and 0.5 mm Hg. The glassy residue was dissolved in 30 ml of dioxane, and 1.5 ml of water was added. Over the course of 10–15 days, a mixture of benzophosphinines **XIIIa, XIVa**, and **XXa**, containing 50–90% of compound **XIIIa**, precipitated. The components were characterized by spectral methods.

Reaction of dioxaphosphole (XVI) with *p*-tolylacetylene was carried out analogously. A mixture of **7-chloro-2-fluoro-4-*p*-tolylbenzo[*e*][1,2λ^5]oxaphosphinine 2-oxide** (**XVIIb**) (50%), **6-bromo-7-chloro-2-fluoro-4-*p*-tolylbenzo[*e*][1,2λ^5]oxaphosphinine 2-oxide** (**XVIIIb**) (35%), and **7-chloro-2-fluoro-4-*p*-tolylbenzo[*e*][1,2λ^5]oxaphosphinine 2-oxide** (**XIXb**) (23%) was obtained. ^{31}P–{^{1}H} NMR spectrum (CH_2Cl_2), δ_P, ppm (*J*, Hz): 2.1 d ($^1J_{PF}$ 1055.0) (**XVIIb**), 1.9 d ($^1J_{PF}$ 1065.0) (**XVIIIb**), and 1.7 d ($^1J_{PF}$ 1069.3) (**XIXb**). The mixture was treated with water in dioxane. Subsequent crystallization gave phosphinine **XIVb** and a mixture of benzophosphorines **XIIIb, XIVb**, and **XXb** in various ratios.

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