ISSN 1070-4280, Russian Journal of Organic Chemistry, 2006, Vol. 42, No. 1, pp. 118–123. © Pleiades Publishing, Inc., 2006.
Original Russian Text © V.F. Mironov, E.N. Varaksina, A.A, Shtyrlina, R.Z. Musin, A.I. Konovalov, 2006, published in Zhurnal Organicheskoi Khimii, 2006, Vol. 42, No. 1, pp. 125–129.

Reactions of Trihalo(phenylenedioxy)phosphoranes with Arylacetylenes: IX.* Reaction of 2,2,2-Trichloro-1,3,2λ^5-benzodioxaphosphole with 1-Iodo-2-phenylethyne

V. F. Mironov, E. N. Varaksina, A. A. Shtyrlina, R. Z. Musin, and A. I. Konovalov

Arbuzov Institute of Organic and Physical Chemistry, Kazan Research Center, Russian Academy of Sciences, ul. Arbuzova 4, Kazan, 420088 Tatarstan, Russia

Received November 22, 2004

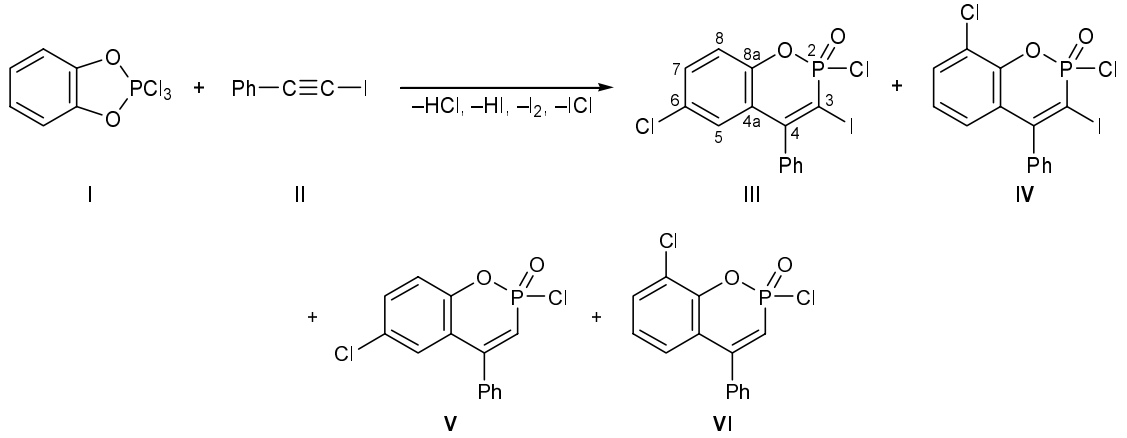
Abstract—According to NMR data, the reaction of 2,2,2-trichloro-1,3,2λ^5-benzodioxaphosphole with 1-iodo-2-phenylethyne leads to formation of 2,6- and 2,8-dichloro-3-iodo-4-phenyl-1,2λ^5-benzoxaphosphinine 2-oxides which undergo partial hydrodeiodination to 2,6- and 2,8-dichloro-4-phenyl-1,2λ^5-benzoxaphosphinine 2-oxides, respectively.

DOI: 10.1134/S1070428006010180

We previously showed that 2,2,2-trichloro-1,3,2λ^5-benzodioxaphosphole (**I**) reacts with monosubstituted arylacetylenes to give unexpected products, derivatives of 4-aryl-2,6-dichloro-1,2λ^5-benzoxaphosphinine 2-oxides, which can be regarded as phosphorus-containing analogs of naturally occurring coumarin [2–7]. The reaction occurs under mild conditions and involves a series of unusual processes, namely facile replacement of one oxygen atom in the phosphole ring, leading to formation of phosphoryl group and phosphorus–carbon bond, and regioselective chlorination of the benzene ring at the *para* position with respect to the oxygen atom in the oxaphosphinine heteroring.

The present communication reports the results of our study on the reaction of trichlorobenzodioxaphosphole **I** with a disubstituted acetylene, 1-iodo-2-phenylethyne (**II**). Compound **I** reacted with **II** in methylene chloride under argon on prolonged keeping of the reaction mixture at 20–25°C (for two months). According to the ^{31}P–{^{1}H} NMR data, the reaction gives four phosphorus-containing compounds with δ 12.48 (*1*), 12.55 (*2*), 16.73 (*3*), and 16.70 ppm (*4*) at a ratio of 1 : 2 : 2 : 4. Signals *3* and *4* are transformed into doublets with coupling constants $^2J_{PH}$ of 24.4 and 24.3 Hz in the spectrum recorded without decoupling from protons. Taking into account published data

Scheme 1.



* For communication VIII, see [1].

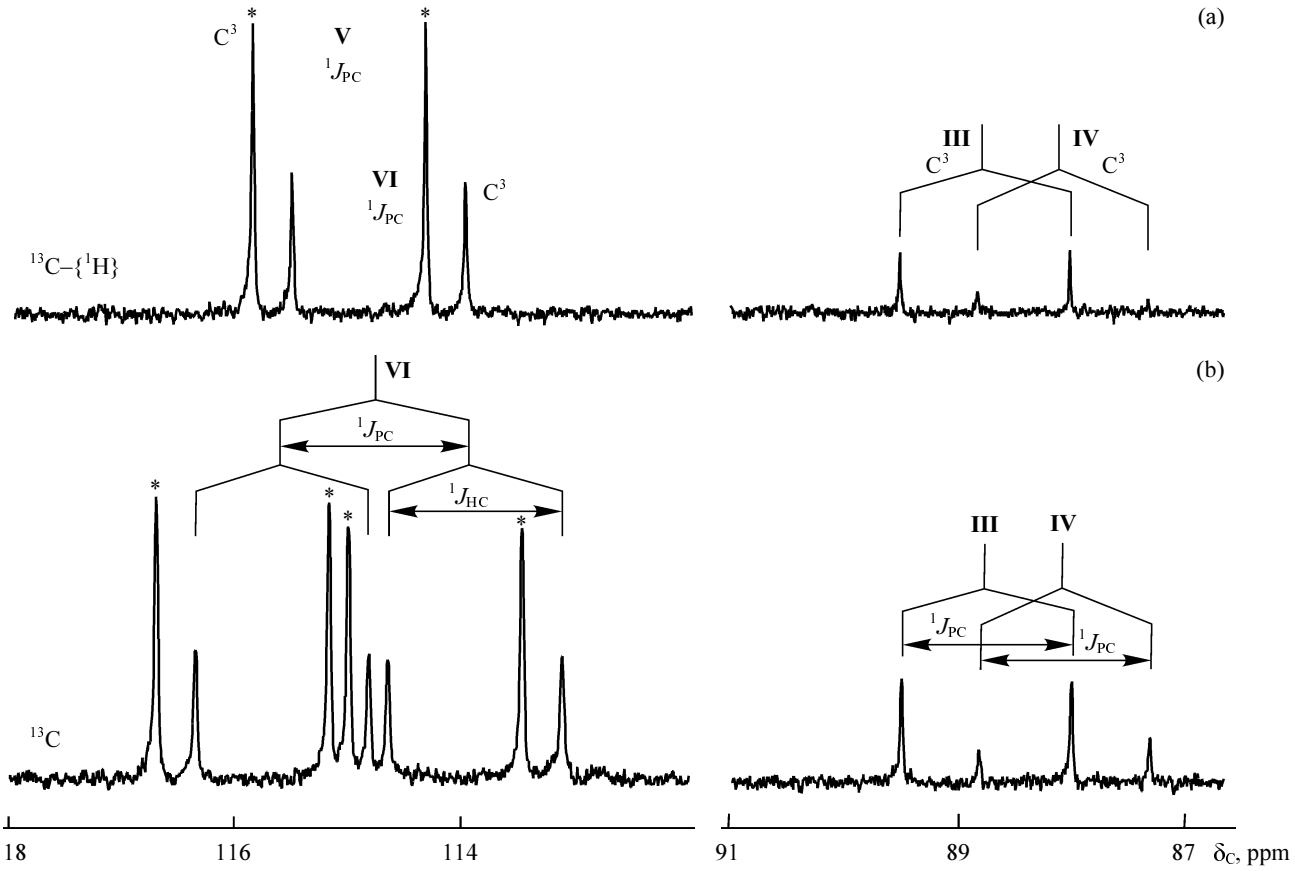


Fig. 1. Upfield regions of the (a) $^{13}C-\{^1H\}$ and (b) ^{13}C NMR spectra ($CDCl_3$) of a mixture of compounds **III**–**VI** freed from volatile substances.

[1–7], we concluded that the products are cyclic phosphonates having P–CH=C and P–C(I)=C fragments.

The mass spectrum (electron impact) of the product mixture obtained after removal of the solvent and volatile compounds under reduced pressure (150°C, 0.1 mm) contained two molecular ion peaks with *m*/*z* 436 and 310. The exact mass values of these ions, 435.8617 and 309.9763 (*m*/*z* values of ions containing the most abundant isotopes), are very consistent with the values 435.8684 and 309.9717, calculated from the assumed elemental compositions $C_{14}H_8Cl_2IO_2P$ and $C_{14}H_9Cl_2O_2P$. These data suggest that the reaction gives isomeric 2-chloro-4-phenyl-1,2λ^5-benzoxaphosphinine 2-oxides **III** (δ_P 12.55 ppm), **IV** (δ_P 12.48 ppm), **V** (δ_P 16.40 ppm), and **VI** (δ_P 16.73 ppm) having a chlorine atom in the fused benzene ring.

The benzoxaphosphinine structure of compounds **III**–**VI** unambiguously follows from the ^{13}C and $^{13}C-\{^1H\}$ NMR spectra. Figure 1 shows the upfield region of the carbon spectra, where resonance of carbon atoms attached to phosphorus is observed. It is seen that all compounds **III**–**VI** give characteristic doublet signals with a direct coupling constant $^1J_{PC}$. The two most upfield signals do not change their multiplicity in going from proton-decoupled to proton-coupled ^{13}C NMR spectrum, i.e., they belong to carbon atoms attached to iodine. The presence of an iodine atom in position *3* of molecules **III** and **IV** strongly affects the chemical shifts of the C^4 and C^9 nuclei (deshielding) and even of the more distant C^{8a} nucleus (shielding) (Fig. 2). Also, increased coupling constant $^2J(P,C^4)$ in iodophosphinines **III** and **IV**, as compared to **V** and **VI**, should be noted (7.9–8.1 against 1.7–1.8 Hz). By contrast, the *trans*-coupling constant $^3J(P,C^9)$ in molecules **V** and **VI** (20.6–20.8 Hz) is larger than in **III** and **IV** (16.5–16.8 Hz), presumably due to difference in the bond angles at the $C^3=C^4$ bond.

Thus the reaction of phosphorane **I** with iodoacetylene **II**, apart from isomeric 3-iodobenzoxaphosphinines **III** and **IV**, yields the corresponding hydrodeiodination products, compounds **V** and **VI**. By special experiment we showed that iodophenylacetylene does not undergo hydrodeiodination by the action of hydro-

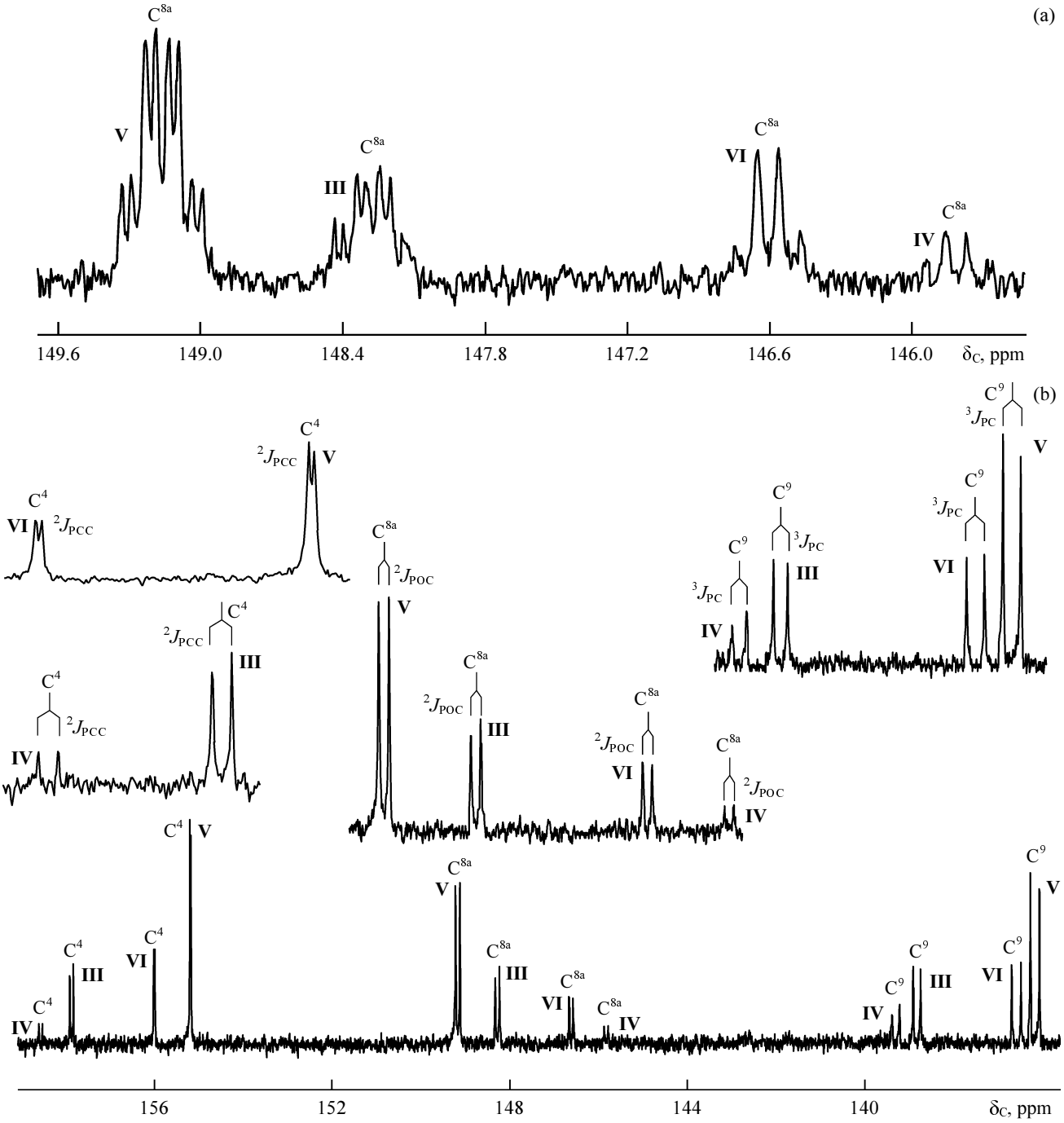
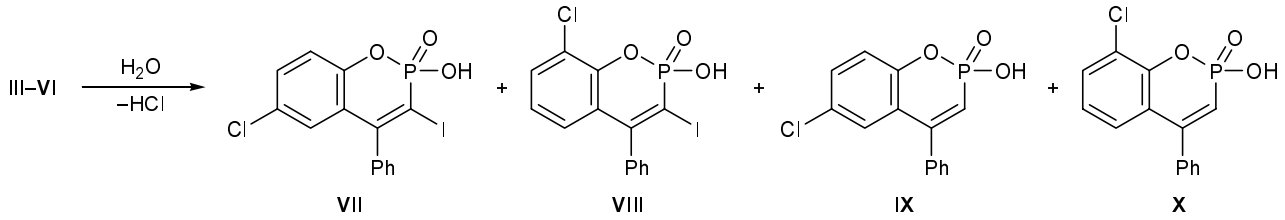


Fig. 2. Downfield regions of the (a) ^{13}C and (b) $^{13}C-\{^1H\}$ NMR spectra ($CDCl_3$) of a mixture of compounds **III**–**VI** freed from volatile substances.

gen chloride liberated due to chlorination of the aromatic ring. Presumably, replacement of iodine by hydrogen occurs during the reaction or in the final products (**III** and **IV**). However, the product ratio almost did not change when the reaction was performed in the presence of pyridine as hydrogen chloride acceptor, but the rate of the process appreciably decreased. Obviously, this problem requires a special study. Replacement of iodine by hydrogen is likely to be accompanied by liberation of HI, ICl, and I_2 which, as well as HCl, could react with excess alkyne **II** to produce a mixture of isomeric styrenes.

In order to determine the position of the chlorine atom in the benzene fragment we analyzed the aromat-

Scheme 2.



ic region of the ^{13}C NMR spectra (Fig. 2; for detailed parameters, see Experimental). Figure 2a shows that the C^{8a} signal of compounds **III** and **V** having a chlorine atom in position 6 is characterized by greater multiplicity (d.d.d.d) due to couplings with the phosphorus atom (^2J), 5-H (^3J), 7-H (^3J), and 8-H (^2J_H); the C^{8a} atom in **IV** and **VI** resonates as a double doublet of doublets with coupling constants similar to those typical of **III** and **V**: $^2J(P,C^{8a})$, $^3J(5\text{-}H,C^{8a})$, and $^3J(7\text{-}H,C^{8a})$. The lack of coupling with 8-H indicates that this position is occupied by chlorine atom. The same also follows from the presence of C^8 signals as characteristic upfield doublets (δ_C 124.10–124.42 ppm, $^3J_{PC}$ = 7.5–8.5 Hz) which show no additional splitting in the proton-coupled spectrum (due to direct interaction $^1J_{CH}$ observed in the spectrum for **IV** and **VI**). Signals from the 4-phenyl substituent were reliably assigned only for the major component (compound **V**). The corresponding signals of compounds **III**, **IV**, and **VI** were difficult to assign, for their concentrations in the mixture were comparable and the signals were overlapped.

Thus, unlike phenylacetylene, the reaction of iodophenylacetylene (**II**) with phosphorane **I** is accompanied by chlorination of the benzene fragment at both *para* and *ortho* positions with respect to the oxygen atom in the oxaphosphinine ring.

We tried to isolate some products as individual compounds. For this purpose, the mixture containing compounds **III**–**VI** was subjected to hydrolysis which led to formation of a mixture of the corresponding phosphonic acids **VII**–**X** at the same ratio (Scheme 2). By crystallization from different solvents (see Experimental) we succeeded in isolating 6-chloro derivatives **VII** and **IX**. The structure of hydroxybenzoxaphosphinines **VII** and **IX** was proved by the ^{31}P, ^1H, and ^{13}C (for **IX**) NMR spectra. The ^{31}P NMR spectrum of 6-chloro-2-hydroxy-3-iodo-4-phenyl-1,2λ^5-benzoxaphosphinine 2-oxide (**VII**) contained a singlet at δ_P –3.1 ppm, while in the ^1H NMR spectrum of **VII** only aromatic proton signals were present.

Thus we were the first to demonstrate the possibility for formation of 1,2λ^5-benzoxaphosphinine derivatives in the reaction of 2,2,2-trichloro-1,3,2λ^5-benzodioxaphosphole with 1-iodo-2-phenylethyne. The reaction is accompanied by unusual replacement of the iodine atom in position *3* by hydrogen and chlorination of the benzo fragment at both *para* and *ortho* positions with respect to the oxygen atom in the oxaphosphinine ring.

EXPERIMENTAL

The NMR spectra were recorded on Bruker MSL-400 (^{13}C, ^{13}C–{^1H}, 100.6 MHz; ^{31}P, ^{31}P–{^1H}, 162.0 MHz) and Bruker WM-250 (^1H, 250 MHz) instruments using HMDS as internal reference for ^1H and ^{13}C and H_3PO_4 as external reference for ^{31}P. The ^1H and ^{13}C NMR spectra were measured at 40–45°C in DMSO-d_6 or C_2D_5OD–DMSO-d_6 or at 25°C in $CDCl_3$. The IR spectra were obtained on a Specord 75IR spectrometer from samples dispersed in mineral oil. The mass spectra were run on an MKh-1310 high-resolution mass spectrometer coupled with an SM-4 computer (energy of ionizing electrons 70 eV, electron collector current 30 μA); samples were introduced directly into the ion source at 120°C. The exact mass values were determined relative to perfluorokerosene; the error did not exceed 5×10^{-5} a.m.u.

Reaction of 2,2,2-trichloro-1,3,2λ^5-benzodioxaphosphole (I) with 1-iodo-2-phenylacetylene (II). A mixture of 3.9 g (0.016 mol) of trichlorophosphorane **I** and 7.2 g (0.032 mol) of iodophenylacetylene in 10 ml of methylene chloride was kept for 2 months at 20–25°C under argon in the dark. The mixture turned dark. The solvent was removed under reduced pressure (12 mm), the residue was washed with a large amount of pentane containing 10% of methylene chloride to remove excess acetylene and chloroiodostyrenes, the washings were removed by decanting, and the residue was dried at 150°C under reduced pressure (0.1 mm). The product was a dark glassy material which contained 2,6-dichloro-3-iodo-4-phenyl-1,2λ^5-benzodioxaphosphinine 2-oxide (**III**), 2,8-dichloro-3-iodo-4-

phenyl-1,2λ^5-benzodioxaphosphinine 2-oxide (**IV**), 2,6-dichloro-4-phenyl-1,2λ^5-benzodioxaphosphinine 2-oxide (**V**), and 2,8-dichloro-4-phenyl-1,2λ^5-benzodioxaphosphinine 2-oxide (**VI**) at a ratio of 2:1:4:2. ^{31}P NMR spectrum (162.0 MHz, $CDCl_3$), δ, ppm (*J*, Hz): 12.55 s (**III**), 12.48 s (**IV**), 16.70 d ($^2J_{PH}$ = 24.3) (**V**), 16.73 d ($^2J_{PH}$ = 24.4) (**VI**). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm (*J*, Hz): compound **III**: 88.67 d (d)** (C^3, $^1J_{CP}$ = 151.3), 157.78 m (d) (C^4, $^2J_{CP}$ = 7.9), 122.93 br.d.d (d) (C^{4a}, $^3J_{CP}$ = 15.9, $^3J_{CH}$ = 5.0), 130.26 m (d) (C^6, $^5J_{PC}$ = 1.4), 131.74 d.d (s) (C^7, $^1J_{CH}$ = 170.1, $^3J_{CH}$ = 5.5–6.0), 120.30 d.d (d) (C^8, $^1J_{CH}$ = 169.0, $^3J_{CP}$ = 8.6), 148.20 d.d.d.d (d) (C^{8a}, $^3J_{C,7\text{-}H}$ = 9.6, $^3J_{C,5\text{-}H}$ = 9.6, $^2J_{CP}$ = 9.5, $^2J_{CH}$ = 4.0), 138.75 d.t (d) (C^i, $^3J_{CP}$ = 16.5, $^3J_{CH}$ = 7.6–7.7); compound **IV**: 87.99 d (d) (C^3, $^1J_{CP}$ = 151.9), 158.47 m (d) (C^4, $^2J_{CP}$ = 8.1), 122.87 br.d.d (d) (C^{4a}, $^3J_{CP}$ = 16.3, $^3J_{CH}$ = 8.3), 124.91 br.d (d) (C^6, $^1J_{CH}$ = 166.5, $^5J_{CP}$ = 1.2), 132.41 d.d (s) (C^7, $^1J_{CH}$ = 167.9, $^3J_{CH}$ = 9.1), 124.10 m (d) (C^8, $^3J_{CP}$ = 8.5), 145.74 d.d.d (d) (C^{8a}, $^3J_{C,7\text{-}H}$ = 8.9–9.1, $^3J_{C,5\text{-}H}$ = 8.9–9.1, $^2J_{CP}$ = 8.5), 139.22 d.t (d) (C^i, $^3J_{CP}$ = 16.8, $^3J_{CH}$ = 7.0–7.5); compound **V**: 115.01 d.d (d) (C^3, $^1J_{CP}$ = 153.9, $^1J_{CH}$ = 171.0), 155.10 m (d) (C^4, $^2J_{CP}$ = 1.7), 122.31 br.d.d.d (d) (C^{4a}, $^3J_{CP}$ = 17.7, $^3J_{C,3\text{-}H}$ = 7.5, $^3J_{C,8\text{-}H}$ = 6.1), 128.89 br.d.d (d) (C^5, $^1J_{CH}$ = 167.7, $^3J_{CH}$ = 5.3, $^4J_{CP}$ = 1.5), 128.25 br.d.m (d) (C^6, $^3J_{CH}$ = 10.7, $^5J_{CP}$ = 1.1), 131.79 d.d (s) (C^7, $^1J_{CH}$ = 169.6, $^3J_{CH}$ = 6.0), 120.74 d.d (d) (C^8, $^1J_{HC}$ = 168.2, $^3J_{CP}$ = 8.1), 149.09 d.d.d.d (d) (C^{8a}, $^3J_{C,7\text{-}H}$ = 10.0, $^3J_{C,5\text{-}H}$ = 10.0, $^2J_{CP}$ = 10.0, $^2J_{CH}$ = 4.2), 136.09 d.t.d (d) (C^i, $^3J_{CP}$ = 20.6, $^3J_{C,m\text{-}H}$ = 7.4, $^3J_{C,3\text{-}H}$ = 6.5), 127.89 d.d.d (d) (C^o, $^1J_{CH}$ = 161.9, $^3J_{CH}$ = 6.3, 6.3–6.4), 128.68 d.d (s) (C^m, $^1J_{CH}$ = 162.5, $^3J_{CH}$ = 6.6), 129.75 d.t (s) (C^p, $^1J_{CH}$ = 162.0, $^3J_{CH}$ = 7.4); compound **VI**: 114.66 d.d (d) (C^3, $^1J_{CP}$ = 154.2, $^1J_{CH}$ = 171.3), 155.91 m (d) (C^4, $^2J_{CP}$ = 1.8), 122.63 br.d.d.d (d) (C^{4a}, $^3J_{CP}$ = 16.7, $^3J_{C,3\text{-}H}$ = 8.3, $^3J_{C,5\text{-}H}$ = 8.3), 124.55 d (s) (C^6, $^1J_{CH}$ = 166.1), 132.49 d.d (s) (C^7, $^1J_{CH}$ = 167.9, $^3J_{CH}$ = 8.6), 124.42 d.d.d (d) (C^8, $^3J_{CH}$ = 9.5–10.0, $^3J_{CP}$ = 7.8, $^2J_{CH}$ = 3.5–4.0), 146.53 d.d.d (d) (C^{8a}, $^3J_{C,7\text{-}H}$ = 9.2, $^3J_{C,5\text{-}H}$ = 9.2, $^2J_{CP}$ = 9.2), 136.51 d.t.d (d) (C^i, $^3J_{CP}$ = 20.8, $^3J_{C,m\text{-}H}$ = 7.0–7.2, $^3J_{C,3\text{-}H}$ = 6.2–6.4).

The obtained mixture of benzoxaphosphinines **III**–**VI** was subjected to hydrolysis via dissolution in aqueous acetone. After 24 h, the crystals were filtered, washed with diethyl ether, and dried in air. We thus obtained 0.9 g of 6-chloro-2-hydroxy-4-phenyl-1,2λ^5-benzodioxaphosphinine 2-oxide (**IX**), mp 259–261°C. ^{13}C NMR spectrum (ethanol-d_6+10% DMSO), δ_C, ppm (*J*, Hz): 116.36 d.d (d) (C^3, $^1J_{CP}$ = 164.0, $^1J_{CH}$ = 170.0), 152.01 m (d) (C^4, $^2J_{CP}$ = 1.9), 124.08 br.d.d.d.d (d) (C^{4a}, $^3J_{CP}$ = 16.3, $^3J_{C,3\text{-}H}$ = 9.0, $^3J_{C,8\text{-}H}$ = 5.0, $^2J_{CH}$ = 1.4), 128.38 d.d.d.d (d) (C^5, $^1J_{CH}$ = 167.8, $^3J_{CH}$ = 5.8, $^4J_{CP}$ = 1.2, $^4J_{CH}$ = 1.2), 128.25 d.d.d.d.d (d) (C^6, $^3J_{CH}$ = 11.4, $^2J_{CH}$ = 4.5, 3.5, $^5J_{CH}$ = 1.2, $^5J_{CP}$ = 1.1), 131.21 d.d (d) (C^7, $^1J_{CH}$ = 169.0, $^3J_{CH}$ = 6.0), 121.60 d.d (d) (C^8, $^1J_{HC}$ = 167.1, $^3J_{CP}$ = 7.1), 150.64 d.d.d.d (d) (C^{8a}, $^3J_{C,7\text{-}H}$ = 10.2, $^3J_{C,5\text{-}H}$ = 8.7, $^2J_{CP}$ = 7.2, $^2J_{CH}$ = 4.1), 138.55 d.t.d (d) (C^i, $^3J_{CP}$ = 18.5, $^3J_{C,m\text{-}H}$ = 7.0, $^3J_{C,3\text{-}H}$ = 6.3), 128.71 br.d.d.d (d) (C^o, $^1J_{CH}$ = 160.9, $^3J_{CH}$ = 6.9, 6.1, $^4J_{CP}$ = 0.7), 129.31 d.d (s) (C^m, $^1J_{CH}$ = 161.5, $^3J_{CH}$ = 6.8, $^2J_{CH}$ = 2.3), 129.31 d.d.d (s) (C$^{m'}$, $^1J_{CH}$ = 161.2, $^3J_{CH}$ = 6.8, $^2J_{CH}$ = 1.1), 129.61 br.d.t (s) (C^p, $^1J_{CH}$ = 159.0, $^3J_{CH}$ = 7.8). ^{31}P NMR spectrum (36.48 MHz, DMSO-d_6): δ_P 2.5 ppm, d, $^2J_{PH}$ = 18.1 Hz. Found, %: C 57.51; H 4.55; P 10.43. $C_{14}H_{10}ClO_3P$. Calculated, %: C 57.44; H 3.42; P 10.59.

After a week, another portion of crystals (0.55 g) was filtered off from the acetone–diethyl ether filtrate. These crystals were a mixture of compounds **VII** and **IX**. The mother liquor was evaporated to dryness under reduced pressure (12 mm), and the glassy residue was dissolved in chloroform. After prolonged storage (for a month), yellowish crystals separated. The crystals (0.2 g) were filtered off and dried under reduced pressure (12 mm). This product was 6-chloro-2-hydroxy-3-iodo-4-phenyl-1,2λ^5-benzodioxaphosphinine 2-oxide (**VII**), mp 246–248°C. IR spectrum, ν, cm^{-1}: 3205, 3134, 3032 2172, 2063 (CH, OH); 1681, 1573, 1542 (C=C); 1488, 1443, 1395, 1378, 1254, 1215, 1165, 1093, 1030, 1001, 987, 918, 900, 883, 865, 823, 773, 751, 731, 698, 673, 655, 615, 604, 536, 502, 482, 442. ^{1}H NMR spectrum (250 MHz, DMSO-d_6), δ, ppm (*J*, Hz): 7.63 m (*m*-H, $^3J_{HH}$ = 7.0), 7.56 m (*p*-H, $^3J_{HH}$ = 7.0), 7.22 (*o*-H), 7.38 d.d.d (7-H, $^3J_{HH}$ = 8.6, $^4J_{HH}$ = 2.6, $^5J_{HP}$ = 1.1), 7.17 d (8-H, $^3J_{HH}$ = 8.6), 6.62 d (5-H, $^4J_{HH}$ = 2.6). ^{31}P NMR spectrum (162.0 MHz, DMSO-d_6, 40°C), δ_P –3.1 ppm (s). Found, %: C 40.22; H 2.37; Cl 8.75; I 29.95; P 7.51. $C_{14}H_9ClIO_3P$. Calculated, %: C 40.14; H 2.15; Cl 8.48; I 30.33; P 7.41.

This study was performed under financial support by the Russian Foundation for Basic Research (project no. 03-03-32542) and by the Program for Support of Leading Scientific Schools (project no. NSh-123.2003.01).

REFERENCES

1. Mironov, V.F., Shtyrlina, A.A., Varaksina, E.N., Efremov, Yu.Ya., and Konovalov, A.I., *Russ. J. Org. Chem.*, 2004, vol. 40, p. 1798.

** Hereinafter, in parentheses are given the multiplicities of signals in the proton-decoupled spectrum.

2. Mironov, V.F., Konovalov, A.I., Litvinov, I.A., Gubaidullin, A.T., Petrov, R.R., Shtyrlina, A.A., Zyablikova, T.A., Musin, R.Z., Azancheev, N.M., and Il'yasov, A.V., *Russ. J. Gen. Chem*., 1998, vol. 68, p. 1414.
3. Mironov, V.F., Litvinov, I.A., Shtyrlina, A.A., Gubaidullin, A.T., Petrov, R.R., Konovalov, A.I., Azancheev, N.M., and Musin, R.Z., *Russ. J. Gen. Chem*., 2000, vol. 70, p. 1046.
4. Mironov, V.F., Petrov, R.R., Shtyrlina, A.A., Gubaidullin, A.T., Litvinov, I.A., Musin, R.Z., and Konovalov, A.I., *Russ. J. Gen. Chem*., 2001, vol. 71, p. 67.
5. Mironov, V.F., Petrov, R.R., Shtyrlina, A.A., Litvinov, I.A., Gubaidullin, A.T., Varaksina, E.N., and Konovalov, A.I., *Izv. Ross. Akad. Nauk, Ser. Khim*., 2001, p. 666.
6. Mironov, V.F., Gubaidullin, A.T., Shtyrlina, A.A., Litvinov, I.A., Petrov, R.R., Konovalov, A.I., Dobrynin, A.B., Zyablikova, T.A., Musin, R.Z., and Morozov, V.I., *Russ. J. Gen. Chem*., 2002, vol. 72, p. 1764.
7. Mironov, V.F., Shtyrlina, A.A., Gubaidullin, A.T., Bogdanov, A.V., Litvinov, I.A., Azancheev, N.M., Latypov, Sh.K., Musin, R.Z., and Efremov, Yu.Ya., *Izv. Ross. Akad. Nauk, Ser. Khim*., 2004, p. 186.