Reaction of 4,6-bis(*tert*-butyl)-2,2,2-trichlorobenzo[*d*]-1,3,2-dioxaphosphole with phenylacetylene. *ipso*-Substitution of the *tert*-butyl group

V. F. Mironov, R. R. Petrov, A. A. Shtyrlina, I. A. Litvinov, A. T. Gubaidullin, E. N. Varaksina, and A. I. Konovalov*

A. E. Arbuzov Institute of Organic and Physical Chemistry, Kazan Research Center of the Russian Academy of Sciences, 8 ul. Akad. Arbuzova, 420088 Kazan, Russian Federation. Fax: +7 (843 2) 75 2253. E-mail: mironov@iopc.kcn.ru

The reaction of 4,6-bis(*tert*-butyl)-2,2,2-trichlorobenzo[*d*]-1,3,2-dioxaphosphole with phenylacetylene follows the mechanism of *ipso*-substitution of the *tert*-butyl group that is in *para*-position relative to the endocyclic O atom of the heterocycle, predominantly yielding 8-(*tert*-butyl)-2,6-dichloro-2-oxo-4-phenylbenzo[*e*]-1,2-oxaphosphorinine (NMR data). The structure of its hydrolysis product, 8-(*tert*-butyl)-6-chloro-2-hydroxy-2-oxo-4-phenylbenzo[*e*]-1,2-oxaphosphorinine, was proved by X-ray diffraction analysis.

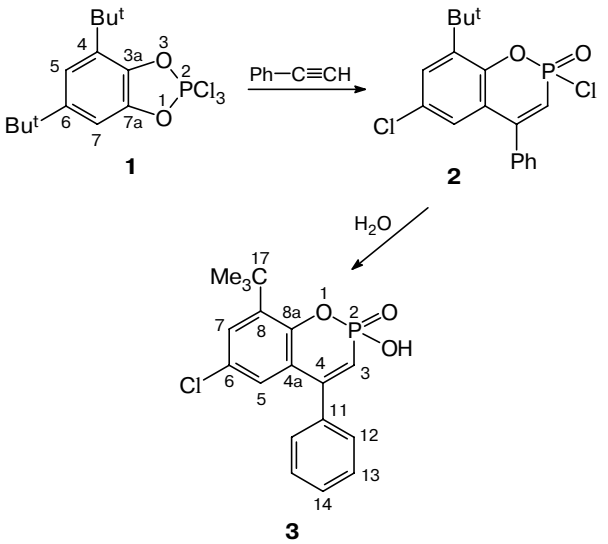
Key words: phenylacetylene, phosphorus(v) chlorides, benzo[*e*]-1,2-oxaphosphorinines, *ipso*-substitution of the *tert*-butyl group, X-ray diffraction analysis.

Recently, we have shown that, unlike PCl_5, phenylenedioxytrichlorophosphorane reacts with arylacetylene to give phosphorus-containing analogs of coumarin, namely, benzo[*e*]-1,2-oxaphosphorinine derivatives in rather high yields.[1,2] It was of interest to involve trichlorophosphoranes with substituents in the benzene ring in this reaction, since in this case it would be possible to study the effect of the corresponding substituents on the reaction outcome and discuss possible pathways for the formation of benzophosphorinines. In the present work, we studied the reaction of the hitherto unknown trichlorophosphorane **1** containing two *tert*-butyl groups with phenylacetylene.

Results and Discussion

Compound **1** readily reacts with phenylacetylene in CH_2Cl_2 with evolution of HCl resulting in a product containing the P(O)CH=C fragment (^{31}P and ^1H NMR data) in 55—65% yield, depending on the degree of dilution. This product was isolated by crystallization from CCl_4, and its structure was established as benzo[*e*]-1,2-oxaphosphorinine **2** based on the ^{13}C NMR spectral data (Table 1). Analysis of the NMR spectra shows that compound **2** contains only one *tert*-butyl group, and the fused benzene ring is tetrasubstituted. Based on the spectroscopic data altogether and the results of our previous publications,[1,2] one can conclude that the Cl atom is in *para*-position relative to the endocyclic O atom of the phosphorinine heterocycle. Thus, the reaction includes *ipso*-substitution for the O atom which is in *meta*-position relative to both *tert*-butyl groups as the main process. In parallel, the *tert*-butyl group that is in *para*-position relative to the O atom of the heterocycle undergoes *ipso*-substitution (Scheme 1).

Scheme 1



This conclusion was completely confirmed by the X-ray diffraction analysis of phosphonic acid **3**, which is a hydrolysis product of chlorophosphorinine **2**. The ^{13}C NMR data for compound **3** and selected geometrical parameters of its molecule are given in Tables 1

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Table 1. ^{31}P, ^{13}C, and ^{13}C-{^1H} NMR parameters for benzophosphorinines **2** and **3** (δ, *J*/Hz)[a]

Atom	**2** (CH_2Cl_2 + 30% C_6D_6)	**3** (DMSO-d_6)
P	15.1 d (J_{PCH} = 24.3)[b]	4.9 d (J_{PCH} = 18)[c]
C(3)	115.3 d (dd, J_{PC} = 155, J_{HC} = 172)	117.1 d (dd, J_{PC} = 169, J_{HC} = 164)
C(4)	156.9 d (m, J_{PCC} = 2)	151.3 d (m, J_{PCC} = 2)
C(4a)	123.9 d (dd, J_{PCCC} = 18, $J_{HC(3)CC}$ = 8)	124.3 d (dd, J_{PCCC} = 16, $J_{HC(3)CC}$ = 8)
C(5)	127.8 s (dd, J_{HC} = 169, $J_{HC(7)CC}$ = 5)	125.8 d (ddd, J_{HC} = 166, $J_{HC(7)CC}$ = 6, J_{POCCC} = 1)
C(6)	130.0 s[d]	126.5 d (br.m, J_{POCCCC} = 1, $J_{HC(7)C}$ = 5, $J_{HC(5)C}$ = 5, $J_{HC(3)CCCC}$ = 1)
C(7)	130.5 s (dd, J_{HC} = 164, $J_{HC(5)CC}$ = 7)	127.8 s (dd, J_{HC} = 165, $J_{HC(5)CC}$ = 6)
C(8)	142.8 d (m, J_{POCC} = 7)	141.6 d (m, J_{POCC} = 6)
C(8a)	149.0 d (ddd, J_{POC} = 11, $J_{HC(7)CC}$ = 9—10, $J_{HC(5)CC}$ = 9—10)	149.1 d (ddd, J_{POC} = 8, J_{HCCC} = 9, J_{HCCC} = 10)
C(11)	137.8 d (m, J_{PCCC} = 21)	138.6 d (ddt, J_{PCCC} = 19, $J_{HC(3)CC(12)}$ = 6, $J_{HC(13)CC}$ = 6—7)
C(12)	128.5 s (br.ddd, J_{HC} = 160, $J_{HC(14)CC}$ = 6—7, $J_{HC(16)CC}$ = 6—7)	128.2 s (ddd, J_{HC} = 161, $J_{HC(14)CC}$ = 7, $J_{HC(16)CC}$ = 6)
C(13)	129.1 s (dd, J_{HC} = 161, $J_{HC(15)CC}$ = 6—7)	128.7 s (dd, J_{HC} = 162, $J_{HC(15)CC}$ = 7)
C(14)	130.1 s (dt, J_{HC} = 161, $J_{HC(12)CC}$ = 6—7)	128.8 s (dt, J_{HC} = 162, $J_{HC(12)CC}$ = 6—7)
C(17)	35.5 s (m)	34.9 s (m, J_{HCC} = 4, J_{HCCC} = 4)
CH_3	29.9 s (qm, J_{HC} = 127, J_{HCCC} = 4)	29.4 s (qm, J_{HC} = 126, J_{HCCC} = 5)

[a] The multiplicities of the ^{31}P or ^{13}C-{^1H} and ^{13}C signals (in parentheses) are indicated.
[b] In CCl_4.
[c] In DMSO.
[d] Overlap with a component of the signal for the C(12) atom.

and 2, respectively. A spatial structure of the molecule in crystal is shown in Fig. 1. Benzophosphorinine **3** contains two planar fragments (O(1)C(8a)C(4a)C(4) and P(2)C(3)C(4)C(4a)) at a dihedral angle of 11.4(1)°. The heterocycle has a distorted boat conformation (the P(2) and C(3) atoms deviate from the O(1)C(8a)C(4a)C(4) plane by −0.5407(7) and −0.227(7) Å, respectively). Note a significant torsion angle between the

Table 2. Selected geometrical parameters of the molecule of benzophosphorinine **3**

Bond	*d*/Å	Bond angle	φ/deg	Torsion angle	τ/deg
Cl(9)—C(6)	1.741(5)	O(1)—P(2)—O(2)	108.0(2)	O(2)—P(2)—O(1)—C(8a)	−155.7(5)
P(2)—O(1)	1.585(3)	O(1)—P(2)—O(3)	105.9(2)	O(3)—P(2)—O(1)—C(8a)	80.4(6)
P(2)—O(2)	1.468(4)	O(1)—P(2)—C(3)	101.9(2)	C(3)—P(2)—O(1)—C(6)	−33.3(6)
P(2)—O(3)	1.514(5)	O(2)—P(2)—O(3)	115.2(2)	O(1)—P(2)—C(3)—C(4)	19.2(6)
P(2)—C(3)	1.744(7)	O(2)—P(2)—C(3)	115.8(3)	O(1)—P(2)—C(3)—H(3)	−156.2(5)
O(1)—C(8a)	1.397(5)	O(3)—P(2)—C(3)	108.8(3)	O(2)—P(2)—C(3)—C(4)	136.2(5)
O(3)—H(30)	0.943(4)	P(2)—O(1)—C(8a)	125.3(3)	O(2)—P(2)—C(3)—H(3)	−39.3(7)
C(3)—H(3)	0.981(6)	P(2)—O(3)—H(30)	111.0(4)	O(3)—P(2)—C(3)—C(4)	−92.3(6)
C(3)—C(4)	1.355(8)	P(2)—C(3)—C(4)	121.7(5)	O(3)—P(2)—C(3)—H(3)	92.3(6)
C(4)—C(4a)	1.477(7)	P(2)—C(3)—H(3)	118.7(5)	P(2)—O(1)—C(8a)—C(4a)	29.7(9)
C(4)—C(11)	1.492(8)	C(3)—C(4)—C(4a)	121.8(5)	P(2)—O(1)—C(6)—C(7)	−153.6(5)
C(4a)—C(5)	1.396(7)	C(3)—C(4)—C(11)	119.1(5)	P(2)—C(3)—C(4)—C(4a)	−2.5(9)
C(4a)—C(8a)	1.379(8)	C(4)—C(4a)—C(8a)	121.7(5)	P(2)—C(3)—C(4)—C(11)	177.5(4)
C(7)—C(6)	1.378(9)	O(1)—C(8a)—C(4a)	119.5(5)	H(3)—C(3)—C(4)—C(4a)	172.9(6)
C(7)—C(8)	1.396(7)	O(1)—C(8a)—C(7)	116.1(5)	C(3)—C(4)—C(5)—C(8a)	−6.7(9)
C(8)—C(17)	1.531(9)	C(8a)—C(8)—C(17)	123.6(5)	C(3)—C(4)—C(5)—C(5)	170.9(6)
C(8a)—C(8)	1.389(8)	C(4)—C(11)—C(12)	119.1(5)	C(11)—C(4)—C(4a)—C(8a)	173.4(6)
C(17)—C(18)	1.505(9)	C(8)—C(17)—C(18)	111.6(5)	C(11)—C(4)—C(4a)—C(5)	−9.1(8)
				C(3)—C(4)—C(11)—C(12)	−64.6(8)
				C(3)—C(4)—C(11)—C(16)	113.2(7)
				C(4)—C(4a)—C(6)—O(1)	−5.8(9)
				C(8a)—C(8)—C(17)—C(18)	178.2(6)
				C(8a)—C(8)—C(17)—C(19)	−63.7(8)
				C(8a)—C(8)—C(17)—C(20)	58.6(8)

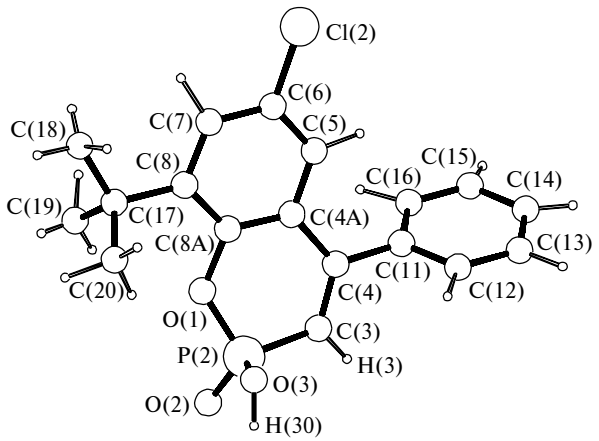

Fig. 1. Structure of compound **3**.

phenyl group and the O(1)C(8a)C(4a)C(4) plane (C(4a)—C(4)—C(11)—C(12) 115.4(6)°). The equatorial O(2) atom and the axial O(3)H(3) group are located at distances of 0.170(5) and −2.037(5) Å, respectively, from the O(1)C(8a)C(4a)C(4) plane. The P(2)—O(2) and P(2)—O(3) bond lengths are markedly different (1.468(4) и 1.514(5) Å, respectively), which makes the P atom chiral. The molecules of **3** crystallize in non-centrosymmetric space group, *i.e.*, they form enantiomers. The absolute configuration of the phosphorus atom is R_P. In general, structure **3** has standard geometrical parameters.[2]

In crystal, the molecules are linked through hydrogen bonds between the hydroxy and phosphoryl groups to form infinite zigzag chains along the crystallographic *y* axis. The O(3)—H(3)...O(2′) ($-x$, $1/2 + y$, $-z$) bond parameters are as follow: the O(3)—H(3), O(3)...O(2′), and H(3)...O(2′) distances are equal to 0.94, 2.514(5), and 1.63 Å, respectively, and the O(3)—H(3)...O(2′) angle is 155°.

Experimental

^{1}H, ^{13}C, ^{13}C-{^{1}H}, ^{31}P, and ^{31}P-{^{1}H} NMR spectra were recorded on Bruker WM-250 (^{1}H, 250 MHz) and Bruker MSL-400 instruments (^{31}P, 162.0 MHz; ^{13}C, 100.6 MHz) in DMSO-d_6 at 45 °C and in C_6D_6—CCl_4 (CH_2Cl_2) at 32 °C with HMDS as the internal standard (^{1}H) and H_3PO_4 as the external standard (^{31}P) or referenced to the residual protons or the carbon nuclei of DMSO and C_6D_6 (^{1}H and ^{13}C). IR spectra were recorded on a Specord IR-75 instrument (suspensions in Vaseline oil).

4,6-Bis(*tert*-butyl)-2,2,2-trichlorobenzo[*d*]-1,3,2-dioxaphosphole (1). 3,5-Bis(*tert*-butyl)pyrocatechol (7 g, 0.032 mol) was added portionwise with stirring to a suspension of PCl_5 (26 g, 0.1247 mol) in 500 mL of benzene over 2 h. The reaction mixture was heated to 50—60 °C to bring the reaction to completion. The solvent was removed under atmospheric pressure, and the residue was distilled *in vacuo*. The yield of phosphorane **1** was 7.33 g (65%), b.p. 139—141 °C (0.1 Torr). Found (%): Cl, 30.04. $C_{14}H_{20}Cl_3O_2P$. Calculated (%): Cl, 29.79. ^{31}P NMR (CH_2Cl_2), δ: −29.2. ^{1}H NMR (CCl_4 + 30% C_6D_6), δ: 1.25, 1.36 (both s, each 18 H, CH_3); 6.88, 6.93 (both br.s, each 2 H, CH). ^{13}C-{^{1}H} NMR (CCl_4 + 30% C_6D_6), δ: 29.94, 31.90 (both s, CH_3); 34.85, 35.56 (both s, C_{quat}); 106.62 (d, C(7), J_{POCC} = 18.0 Hz); 118.12 (s, C(5)); 134.59 (d, C(4), J_{POCC} = 13.9 Hz); 139.17 (s, (C(6)); 143.31 (s, C(3a)); 147.07 (s, C(7a)).

Reaction of phosphorane 1 with phenylacetylene. Dry argon was passed through a solution of phosphorane **1** (7.3 g, 0.02 mol) in 50 mL of CH_2Cl_2, and a solution of phenylacetylene (4.5 mL, 0.04 mol) in 30 mL of CH_2Cl_2 was added dropwise at 5—10 °C. Hydrogen chloride evolved vigorously. The reaction mixture was kept at 20 °C for one day, and the solvent was removed. Then, the excess of phenylacetylene and styryl chloride were removed *in vacuo* (0.1 Torr). The residual light yellow viscous glass was dissolved in CCl_4 and kept for 3—5 days to give 8-(*tert*-butyl)-2,6-dichloro-2-oxo-4-phenylbenzo[*e*]-1,2-oxaphosphorinine (**2**) as a crystalline precipitate, which was filtered off, washed with cold CCl_4, and dried *in vacuo*. Yield 2.33 g (31%), m.p. 196 °C. Found (%): C, 59.07; H, 4.88; P, 8.31; Cl, 19.76. $C_{18}H_{17}Cl_2O_2P$. Calculated (%): C, 58.85; H, 4.63; P, 8.44; Cl, 19.34. ^{1}H NMR (CCl_4 + 30% C_6D_6), δ: 1.30 (s, 9 H, CH_3); 5.84 (d, 1 H, H(3), J_{PCH} = 24.5 Hz); 6.76 (m, 2 H, H_o); 6.96 (d, H(5), $J_{H(7)CCCH(5)}$ = 2.7 Hz); 6.97, 7.02 (both m, each 4 H, H_p, H_m, H(5)); 7.28 (dd, 1 H, H(7), $J_{H(7)CCCH(5)}$ = 2.7 Hz, $J_{POCCCH(7)}$ = 1.5 Hz).

Chlorophosphorinine **2** was dissolved in 20 mL of dioxane and treated with water (0.4 mL). Prolonged storage (>10 days) of the reaction mixture in open air gave 8-(*tert*-butyl)-6-chloro-2-hydroxy-2-oxo-4-phenylbenzo[*e*]-1,2-oxaphosphorinine (**3**) as a well-formed crystalline precipitate, which was filtered off, washed with ether, and dried. Yield 2.0 g (90%), m.p. 212—214 °C. Found (%): C, 62.12; H, 5.19; P, 9.03; Cl, 10.07. $C_{18}H_{18}ClO_3P$. Calculated (%): C, 61.97; H, 5.16; P, 8.89; Cl, 10.18. ^{1}H NMR (CD_3OD), δ: 1.46 (br.s, 9 H, CH_3); 6.22 (d, 1 H, H(3), J_{PCH} = 18.8 Hz); 6.91 (d, 1 H, H(5), $J_{H(7)CCCH(5)}$ = 2.6 Hz); 7.30—7.31, 7.44—7.46 (both m, each 5 H, Ph); 7.37 (dd, 1 H, H(7), $J_{H(7)CCCH(5)}$ = 2.6 Hz, $J_{POCCCH(7)}$ = 1.7 Hz). IR, ν/cm^{-1}: 482, 517, 562, 580, 635, 700, 725, 765, 815, 822, 872, 888, 945, 998, 1000 sh, 1125, 1150, 1180, 1220, 1232 sh, 1270 (P=O); 1335, 1365, 1420, 1452, 1555 (C=C); 1590, 1600, 2130—2150 v.br, 2260—2290 v.br, 2500—2600 v.br.

X-Ray diffraction analysis of compound 3. The crystals of **3** are monoclinic, at 20 °C a = 9.8774(9), b = 5.942(1), c = 16.317(4) Å, β = 97.11(2)°, V = 854.1(3) Å^3, Z = 2, d_{calc} = 1.36 g cm^{-3}, space group $P2_1$, $C_{18}H_{18}ClO_3P$. The unit cell parameters and the intensities of 1978 reflections (including 1147 reflections with $I \geq 3\sigma$) were measured on an Enraf—Nonius CAD4 automated four-circle diffractometer (λMo-Kα, graphite monochromator, ω/2θ scan mode, $\theta \leq 26.9°$). The intensities of three reference reflections were not decreased during recording, and absorption correction (μ-Mo 3.3 cm^{-1}) was not applied. The structure was solved by the direct method with the SIR program[3] and refined first in the isotropic and then anisotropic approximations. The H atoms were located from the difference electron-density map and included with fixed coordinates and isotropic thermal parameters. To establish the absolute structure and configuration of **3**, we refined the "direct" and inverted structures with consideration of abnormal scattering by all non-hydrogen atoms. The discrepancy factors are R = 0.04035 and R_w = 0.04440 for 1065 reflections from the direct structure and R = 0.04039 and R_w = 0.04444 for the inverted structure. According to the Hamilton test,[4] the direct structure corresponds to the absolute structure at a confidence

level of 90%. The final residuals are $R = 0.040$ and $R_w = 0.044$ for 1065 independent reflections with $F^2 \geq 3\sigma$. All calculations were performed with the MOLEN program package[5] using an AlphaStation 200 computer. Intermolecular interactions were analyzed and structure **3** was constructed with the PLATON program.[6] The atomic coordinates were deposited with the Cambridge Crystallographic Database.

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