Reaction of 2,2,2-trichlorobenzo[*d*]-1,3,2-dioxaphosphole-5-carbonylchloride with phenylacetylene: predominant formation of 2-(2-chloro-2-phenylethenyl)-2,2-dichlorobenzo[*d*]-1,3,2-dioxaphosphole-5-carbonylchloride

V. F. Mironov, A. V. Bogdanov, and A. I. Konovalov*

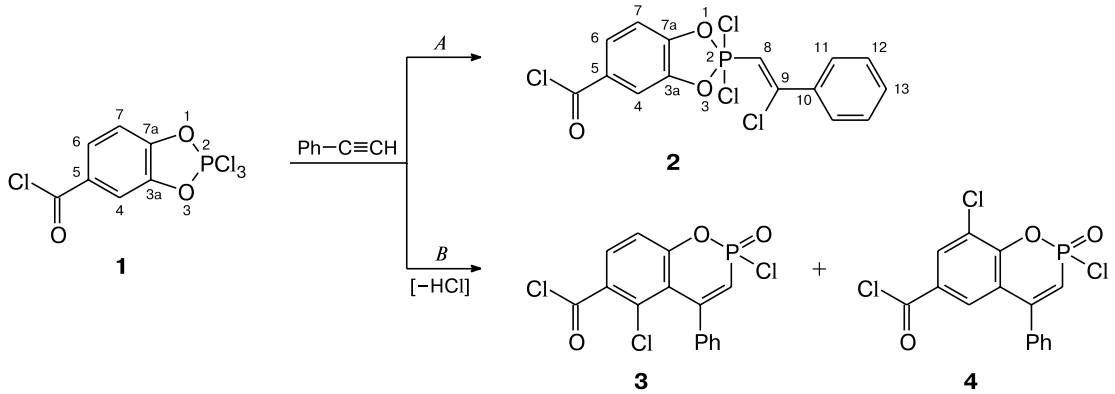
A. E. Arbuzov Institute of Organic and Physical Chemistry,
Kazan Research Center of the Russian Academy of Sciences,
8 ul. Akad. Arbuzova, 420088 Kazan, Russian Federation.
Fax: +7 (843 2) 73 2253. E-mail: mironov@iopc.knc.ru

The reaction of 2,2,2-trichlorobenzo[*d*]-1,3,2-dioxaphosphole-5-carbonylchloride with phenylacetylene in benzene (80 °C) afforded 2-(2-chloro-2-phenylethenyl)-2,2-dichlorobenzo[*d*]-1,3,2-dioxaphosphole-5-carbonylchloride (yield >95%) as a result of the electrophilic *cis*-addition of the phosphorus(v) derivative at the triple bond of acetylene with retention of coordination of the P atom. Hydrolysis of this compound affords predominantly 2-hydroxy-5-(hydroxycarbonyl)phenyl (2-chloro-2-phenylethenyl)phosphonate.

Key words: phenylacetylene, phosphorus(v) chlorides, benzo[*d*]-1,3,2-dioxaphospholes, electrophilic addition, hydrolysis of phosphoranes.

The reactions of phosphorus pentachloride with acetylenes provide one of the most important methods for the synthesis of unsaturated phosphonic acids, which have attracted considerable recent attention due to high and various biological activities.[1,2] Recently, we have demonstrated[3,4] that the closest stable analog of phosphorus pentachloride, *viz.*, 2,2,2-trichlorobenzo[*d*]-1,3,2-dioxaphosphole, reacts with arylacetylenes to form phosphorus-containing analogs of coumarins and α-chromenes, *viz.*, benzo[*e*]-1,2-oxaphosphorinines. Depending on the nature of substituents in the benzo fragment, the reaction is accompanied also by chlorination of the latter in the *para* or *meta* position relative to the endocyclic oxygen atom of the oxaphosphorinine heterocycle.[5—7] The reaction of the phosphorylated derivative of natural protocatechuic acid, *viz.*, 2,2,2-trichlorobenzo[*d*]-1,3,2-dioxaphosphole-5-carbonylchloride (**1**), with phenylacetylene follows two pathways (Scheme 1), such as the classical electrophilic *cis*-addition at the triple bond of acetylene with retention of coordination of the phosphorus atom to form 2-(2-chloro-2-phenylethenyl)-2,2-dichlorobenzo[*d*]-1,3,2-dioxaphosphole-5-carbonylchlo-

Scheme 1



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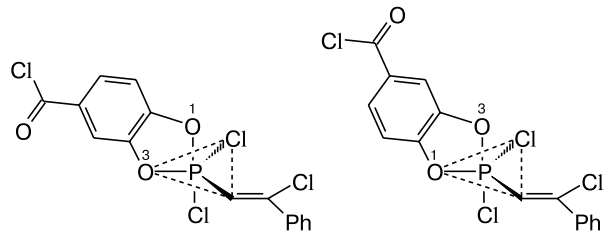
ride (**2**) (*A*) and the formation of benzooxaphosphorinines **3** and **4** (*B*).[8] Since the percentage of product **2** was no higher than 20%, it was not isolated in pure form.

In the present study, we demonstrated that, by changing the reaction conditions (the addition of phenylacetylene to a refluxing solution of phosphorane **1** in benzene), the reaction can be made to follow only the pathway *A*, *i.e.*, phosphorane **2** can be selectively prepared (according to the $^{13}C—\{^1H\}$ and $^{31}P—\{^1H\}$ NMR spectroscopic data, the yield of **2** in the crude material was >95%). Based on the constant $J_{P,C(8),C,C(10)} = 23.4$ Hz characteristic of the *trans* orientation of the P and C(10) atoms, the *Z* configuration was assigned to the reaction product.

Therefore, the electrophilic addition can be made the main reaction pathway by increasing the temperature and changing the order of mixing of the reagents. However, this is not associated with the kinetic and thermodynamic control. Both independent (competitive) reactions irreversibly afford stable compounds **2—4**. Apparently, the activation energy of the rate-determining step of the first process at 10—20 °C is higher than that of the second process.

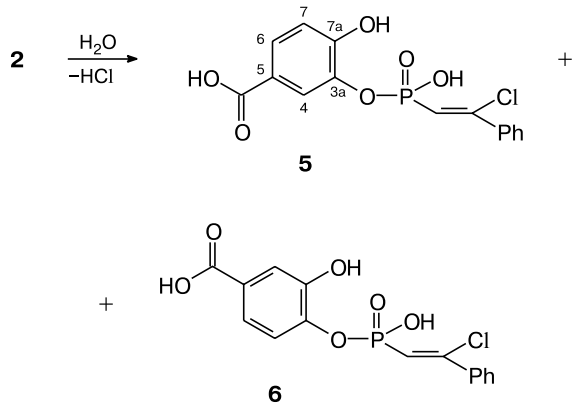
Since phosphorane **2** contains two nonequivalent oxygen atoms (the electron-withdrawing substituent COCl is present in the *para* position with respect to the O(1) atom), the signals for the carbon atoms of the benzo fragment (for the apical arrangement of the O(1) and O(3) atoms in forms **A** and **B**) would be expected to be doubled in the ^{13}C NMR spectra. However, no doubling is observed due, apparently, to either a rapid pseudotransformation, resulting in averaging of the signals of forms **A** and **B**, or a substantially higher apicophility of the O(1) atom (form **A**).



Mild hydrolysis of phosphorane **2** in diethyl ether in air affords a mixture of phosphonates **5** and **6** in a ratio of 8 : 1 (Scheme 2).

The structures of compounds **5** and **6** were established by ^1H NMR spectroscopy. The structure of phosphonate **5** was additionally confirmed by ^{13}C NMR spectroscopy. The ring opening leads to the disappearance of spin-spin coupling between the phosphorus atom and the C(7) and C(7a) nuclei in compound **5**, which confirms the fact that hydrolysis occurs predominantly at the P—O(1) bond. We failed to separate regioisomer **5** from an impurity of

Scheme 2



compound **6** by crystallization from different solvents (acetone, dioxane, or benzene).

To summarize, we demonstrated for the first time that the pathway of the reaction of trichlorobenzodioxaphosphole **1** with phenylacetylene substantially depends on the reaction temperature. The rise of the temperature makes it possible to synthesize the addition product at the triple bond of acetylene, *viz.*, dichlorodioxaphosphole **2**, in high yield.

Experimental

The ^1H, ^{13}C, $^{13}C—\{^1H\}$, ^{31}P, and $^{31}P—\{^1H\}$ NMR spectra were recorded on Bruker MSL-400 (400 MHz for ^1H and 100.6 MHz for ^{13}C) and Bruker CXP-100 (36.48 MHz for ^{31}P) instruments in $CDCl_3$ (20 °C) or DMSO-d_6 (45 °C) on the δ scale relative to Me_4Si; the signals of the residual protons of the deuterated solvent or the carbon nuclei of DMSO-d_6 or $CDCl_3$ (^1H and ^{13}C) were used as the internal standard; 85% H_3PO_4 was used as the external standard. The IR spectrum was measured in Nujol mulls on a Bruker Vector-22 Fourier-transform spectrometer.

Compound 2. A solution of phenylacetylene (1.63 g, 0.016 mol) in benzene (10 mL) was added dropwise to a solution of benzodioxaphosphole **1** (4.3 g, 0.014 mol) in benzene (60 mL), into which dry argon was bubbled through a thin capillary, at 80 °C. The solvent was then removed from the reaction mixture by distillation. A viscous glassy pale-yellow residue was dried *in vacuo* (0.1 Torr) at 40—50 °C to remove an excess of phenylacetylene and residual benzene. The yield was 5.50 g (96%). Found (%): Cl, 35.07. $C_{15}H_9Cl_4O_3P$. Calculated (%): Cl, 34.63. ^{31}P NMR ($CDCl_3$), δ: −15.3 (d, $^2J_{P,H} = 36.5$ Hz). ^1H NMR ($CDCl_3$), δ: 7.01 (d, H(7), $^3J_{H(6),H(7)} = 8.5$ Hz); 7.21 (m, H(13)); 7.29 (d, PCH, $^2J_{P,H} = 37.7$ Hz); 7.36 (m, H(12)); 7.54 (m, H(11)); 7.76 (dd, H(4), $^4J_{H(6),H(4)} = 2.0$ Hz, $^4J_{P,H(4)} = 1.5$ Hz); 7.83 (dd, H(6), $^3J_{H(7),H(6)} = 8.5$ Hz, $^4J_{H(4),H(6)} = 2.0$ Hz). ^{13}C NMR ($CDCl_3$), δ:* 110.95 (dd [s], C(7), $^1J_{H,C(7)} = 169.6$ Hz, $^3J_{P,O,C,C(7)} = 12.4$ Hz); 114.01 (ddd [d], C(4),

* Hereinafter, the multiplicities of the signals in the $^{13}C—\{^1H\}$ NMR spectra are given in brackets.

$^1J_{H,C(4)}$ = 170.0 Hz, $^3J_{P,O,C,C(4)}$ = 16.3 Hz, $^3J_{H,C(6),C,C(4)}$ = 7.0 Hz); 126.81 (dddd [s], C(11), $^1J_{H,C(11)}$ = 161.1 Hz, $^3J_{H,C(11'),C,C(11)}$ = 6.2 Hz, $^3J_{H,C(13),C,C(11)}$ = 6.2 Hz, $^2J_{H,C(12),C(11)}$ = 2.2 Hz); 127.17 (d [s], C(5), $^3J_{H,C(7),C,C(5)}$ = 8.7 Hz); 128.61 (dd [d], C(8), $^1J_{P,C(8)}$ = 201.8 Hz, $^1J_{H,C(8)}$ = 168.8 Hz); 142.0 (ddt [d], C(9), $^2J_{P,C(8),C(9)}$ = 9.4 Hz, $^3J_{H,C(11),C,C(9)}$ = 3.5 Hz, $^2J_{H,C(8),C(9)}$ = 3.0—3.5 Hz); 128.62 (dd [s], C(12), $^1J_{H,C(12)}$ = 161.2 Hz, $^3J_{H,C(12'),C,C(12)}$ = 7.3 Hz); 128.95 (dd [s], C(6), $^1J_{H,C(6)}$ = 166.8 Hz, $^3J_{H,C(4),C,C(6)}$ = 6.0 Hz); 131.12 (dt [s], C(13), $^1J_{H,C(13)}$ = 162.1 Hz, $^3J_{H,C(11),C,C(13)}$ = 7.5 Hz); 134.70 (dtd [d], C(10), $^3J_{P,C(8),C,C(10)}$ = 23.4 Hz, $^3J_{H,C(12),C,C(10)}$ = 7.1 Hz, $^3J_{H,C(8),C,C(10)}$ = 3.5 Hz); 142.36 (dd [s], C(3a), $^3J_{H,C(7),C,C(3a)}$ = 6.1 Hz, $^2J_{H,C(4),C(3a)}$ = 5.5 Hz); 150.38 (ddd [s], C(7a), $^3J_{H,C(4),C,C(7a)}$ = 10.7 Hz, $^3J_{H,C(6),C,C(7a)}$ = 6.7 Hz, $^2J_{H,C(7),C(7a)}$ = 2.7 Hz); 166.23 (dd [s], COCl, $^3J_{H,C(6),C,C}$ = 5.1 Hz, $^3J_{H,C(4),C,C}$ = 5.1 Hz).

Hydrolysis of compound 2. Wet nitrogen was bubbled through a thin capillary into a solution of compound **2** (5.0 g, 0.012 mol) in diethyl ether (40 mL) until HCl evolution ceased. The white precipitate that formed was filtered off, washed with cold (0 °C) diethyl ether, and dried in air. A mixture of regioisomeric 2-hydroxy-5-(hydroxycarbonyl)phenyl (2-chloro-2-phenylethenyl)phosphonate (**5**) and 2-hydroxy-4-(hydroxycarbonyl)phenyl (2-chloro-2-phenylethenyl)phosphonate (**6**) in a ratio of 8 : 1 was obtained in a yield of 3.8 g (88%). Found (%): C, 51.01; H, 3.73; P, 8.65. $C_{15}H_{12}ClO_6P$. Calculated (%): C, 50.77; H, 3.38; P, 8.74. IR, ν/cm^{-1}: 3265 br, 3059 br, 2671 br, 2240 v.br, 1696, 1614, 1596, 1576, 1520, 1414, 1180, 1124, 1096, 1010, 981, 909, 884, 752. ^{31}P NMR of compound **5** (DMSO-d_6), δ: 6.9 (d, $^2J_{P,C,H}$ = 8.3 Hz). ^{1}H NMR of compound **5** (DMSO-d_6), δ: 6.82 (d, 1 H, PCH, $^2J_{P,C,H}$ = 8.2 Hz); 7.03 (d, 1 H, H(7), $^3J_{H(6),H(7)}$ = 8.5 Hz); 7.44—7.46 (m, 3 H, H(12), H(13)); 7.61 (dd, 1 H, H(6), $^3J_{H(7),H(6)}$ = 8.5 Hz, $^4J_{H(4),H(6)}$ = 2.0 Hz); 7.69 (m, 2 H, H(11), $^3J_{H(11),H(12)}$ = 7.6 Hz); 7.84 (dd, 1 H, H(4), $^4J_{H(6),H(4)}$ = 2.0 Hz, $^4J_{P,H(4)}$ = 1.7—1.8 Hz); 12.42 (br.s, 2 OH). ^{13}C NMR of compound **5** ($CDCl_3$), δ: 117.40 (br.d [s], C(7), $^1J_{H,C(7)}$ = 162.2 Hz); 117.78 (dd [d], C(8), $^1J_{P,C(8)}$ = 194.4 Hz, $^1J_{H,C(8)}$ = 147.3 Hz); 122.39 (br.d [s], C(5), $^3J_{H,C(7),C,C(5)}$ = 8.7 Hz); 123.92 (ddd [br.d], C(4), $^1J_{H,C(4)}$ = 163.3 Hz, $^3J_{H,C(6),C,C(4)}$ = 7.0 Hz, $^3J_{P,O,C,C(4)}$ = 3.0 Hz); 127.29 (ddd [s], C(11), $^1J_{H,C(11)}$ = 160.9 Hz, $^3J_{H,C,C,C(11)}$ = 5.7 Hz, $^3J_{H,C,C,C(11)}$ = 7.1 Hz); 127.73 (br.d [s], C(6), $^1J_{H,C(6)}$ = 166.4 Hz, $^3J_{H,C(4),C,C(6)}$ = 7.5 Hz); 129.36 (dd [s], C(12), $^1J_{H,C(12)}$ = 163.7 Hz, $^3J_{H,C(12'),C,C(12)}$ = 6.6 Hz); 131.32 (dt [s], C(13), $^1J_{H,C(13)}$ = 162.5 Hz, $^3J_{H,C(11),C,C(13)}$ = 7.2 Hz); 137.07 (m [d], C(10), $^3J_{P,C(8),C,C(10)}$ = 16.7 Hz); 138.71 (m [d], C(9), $^2J_{P,C(8),C(9)}$ = 7.4 Hz); 147.10 (m [d], C(7a), $^3J_{H,C(4),C,C(7a)}$ = 5.0—6.0 Hz, $^3J_{H,C(6),C,C(7a)}$ = 5.0—6.0 Hz, $^3J_{P,O,C,C(7a)}$ = 1.4 Hz); 153.60 (m [d], C(3a), $^2J_{P,O,C(3a)}$ = 5.0 Hz); 167.25 (dd [s], COOH, $^3J_{H,C(6),C,C}$ = 3.6 Hz, $^3J_{H,C(4),C,C}$ = 3.6 Hz). ^{31}P NMR of compound **6** (DMSO-d_6), δ: 6.6 (d, $^2J_{P,C,H}$ = 8.3 Hz). ^{1}H NMR of compound **6** ($CDCl_3$), δ: 6.83 (d, 1 H, PCH, $^2J_{P,C,H}$ = 8.3 Hz); 7.31 (dd, H(7), $^3J_{H(6),H(7)}$ = 8.4 Hz, $^4J_{P,H(7)}$ = 1.3 Hz); 7.38 (dd, H(6), $^3J_{H(7),H(6)}$ = 8.4 Hz, $^4J_{H(4),H(6)}$ = 2.0 Hz); 7.42—7.45 (m, H(12), H(13)); 7.54 (d, H(4), $^4J_{H(6),H(4)}$ = 2.0 Hz); 7.69 (m, H(11)); 12.40 (br.s, OH).

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