ISSN 1070-4280, Russian Journal of Organic Chemistry, 2007, Vol. 43, No. 11, pp. 1737–1739. © Pleiades Publishing, Ltd., 2007.
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SHORT COMMUNICATIONS

Regioselectivity of the Reaction of 4,6-Di-*tert*-butyl-2,2,2-trichloro-1,3,2λ^5-benzodioxaphosphole with Hex-1-yne. *ipso* Substitution of *tert*-Butyl Group

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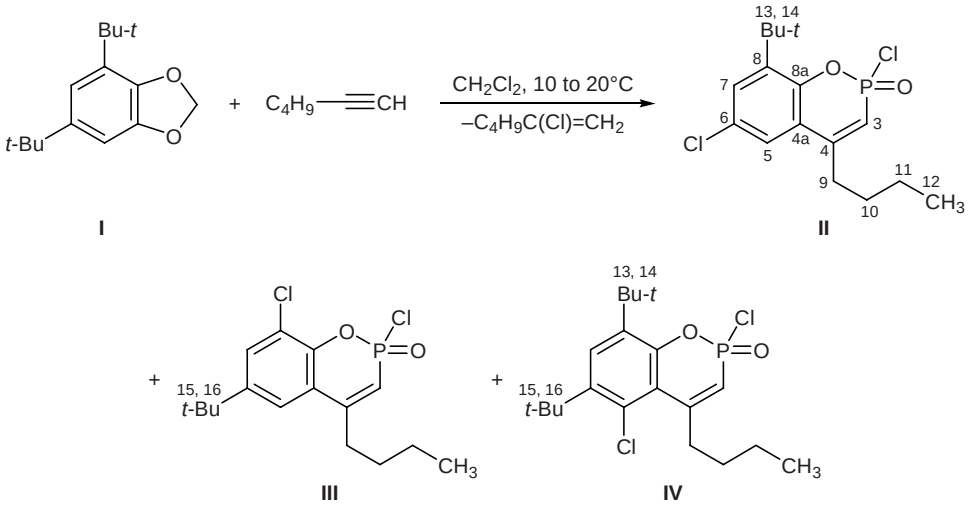
Received October 3, 2006

DOI: 10.1134/S1070428007110280

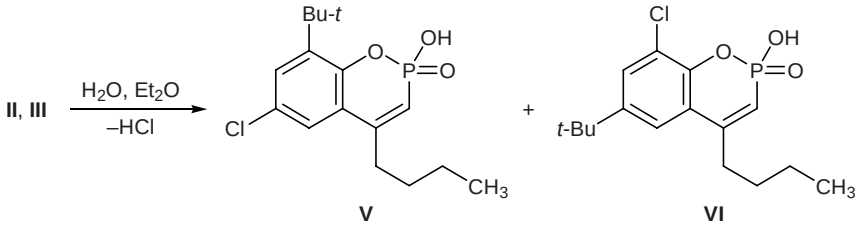
Unlike phosphorus pentachloride, 2,2,2-trichloro-1,3,2λ^5-benzodioxaphosphole reacts with 1-hexyne to give 1,2λ^5-benzoxaphosphinine derivatives [1] that can be regarded as phosphorus-containing analogs of biologically important coumarins and α-chromenes [2]; this reaction considerably extends the scope of the procedure described in [3]. We now report that 4,6-di-*tert*-butyl-2,2,2-trichloro-1,3,2λ^5-benzodioxaphosphole (**I**) having bulky *tert*-butyl groups is also capable of reacting with 1-hexyne under mild conditions to give exclusively 1,2λ^5-benzoxaphosphinine derivatives which show in the ^{31}P NMR spectra doublets at δ_P 18.5–19.1 ppm ($^2J_{PH}$ = 24.1–27.3 Hz).

Analysis of the ^{13}C and ^{13}C-{^{1}H} NMR spectra of the reaction mixture (after removal under reduced pressure of the solvent and 2-chlorohex-1-ene formed by addition of liberated hydrogen chloride to the initial alkyne) showed that the reaction gives a mixture of benzoxaphosphinines **II**–**IV** (Scheme 1). These compounds display characteristic doublets from the C^3, C^{4a}, C^8, C^{8a}, and C^9 nuclei in the ^{13}C NMR spectra. On the basis of multiplicities of the corresponding signals in the ^{13}C–{^{1}H} NMR spectrum we unambiguously assigned structures of products **II**–**IV**. The major of these is compound **II** which results from replacement of the oxygen atom in the *meta* position with respect to the *tert*-butyl group and substitution of the *tert*-butyl group in the *para* position with respect to the oxygen atom; the yield of **II** exceeds 70%. Minor 1,2λ^5-benzoxaphosphinines **III** and **IV** are formed in approximately equal amounts. The structure of compounds **III** and **IV** was confirmed by the ^{13}C NMR spectra of their

Scheme 1.



Scheme 2.



hydrolysis products **V** and **VI** which were isolated as individual substances (Scheme 2).

Reaction of 4,6-di-*tert*-butyl-2,2,2-trichloro-1,3,2λ^5-benzodioxaphosphole (I) with hex-1-yne. A mixture of 4.5 g (0.0126 mol) of phosphole **I**, 5 ml of methylene chloride, and 2.2 ml (1.57 g, 0.019 mol) of hex-1-yne was kept for 12 h at 10–20°C. The solvent, excess alkyne, and 2-chlorohex-1-ene were removed under reduced pressure (12 mm) at 130°C. The residue, a light brown glassy material, was a mixture of benzoxaphosphinines **II**–**IV**.

4-Butyl-8-*tert*-butyl-2,6-dichloro-1,2λ^5-benzoxaphosphinine 2-oxide (II). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 6.33 d (3-H, $^2J_{PH}$ = 24.1), 7.47 d and 7.49 d (7-H, 5-H, $^4J_{5,7}$ = 1.7), 2.73 m (9-H, *AB* part of *ABX*$_2$ spin system), 1.66 m (10-H), 1.49 m (11-H), 0.99 t (12-H, ^3J = 7.3), 1.48 s (14-H). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm (*J*, Hz) (hereinafter, in parentheses is given the signal multiplicity in the ^{13}C–{^{1}H} NMR spectrum): 113.28 d.d.t (d) (C^3, $^1J_{CP}$ = 157.4, $^1J_{CH}$ = 169.6, $^3J_{CH}$ = 6.0), 156.82 m (s) (C^4), 123.09 d.d.t.d (d) (C^{4a}, $^3J_{CP}$ = 18.0, $^3J_{CH}$ = 7.8, $^3J_{CH}$ = 3.1, $^2J_{CH}$ = 0.9), 124.37 d.d (s) (C^5, $^1J_{CH}$ = 165.8, $^3J_{CH}$ = 5.4), 130.02 d.d (s) (C^6, $^2J_{CH}$ = 4.8, 4.4), 129.89 d.d (s) (C^7, $^1J_{CH}$ = 165.4, $^3J_{CH}$ = 5.8), 142.53 d (d) (C^8, $^3J_{CP}$ = 7.4), 148.52 d.d.d (d) (C^{8a}, $^3J_{CH}$ = 10.4, 10.4, $^2J_{CP}$ = 11.4), 35.04 t.d.m (d) (C^9, $^3J_{CP}$ = 19.8, $^1J_{CH}$ = 127.8, $^3J_{CH}$ = 5.6–6.0, 3.9–4.0, $^2J_{CH}$ = 3.9–4.0), 30.08 t.m (s) (C^{10}, $^1J_{CH}$ = 126.6, $^3J_{CH}$ = 3.9-4.2, $^2J_{CH}$ = 3.9–4.2), 22.28 t.m (s) (C^{11}, $^1J_{CH}$ = 125.3, $^3J_{CH}$ = 3.2–3.5, $^2J_{CH}$ = 3.2–3.5), 13.80 q.m (s) (C^{12}, $^1J_{CH}$ = 125.1, $^2J_{CH}$ = 3.9–4.1, 3.9–4.1), 35.43 m (s) (C^{13}), 29.83 q.sept (s) (C^{14}, $^1J_{CH}$ = 126.7, $^3J_{CH}$ = 4.6). Mass spectrum, *m*/*z*: 346, 348, 350 $[M]^{+\cdot}$. $C_{16}H_{21}Cl_2O_2P$.

4-Butyl-6-*tert*-butyl-2,8-dichloro-1,2λ^5-benzoxaphosphinine 2-oxide (III). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 6.48 d (3-H, $^2J_{PH}$ = 27.3), 7.62 s (7-H), 2.85 br.d.d.d and 3.22 br.d.d.d (9-H$_A$, 9-H$_X$, $^2J_{AX}$ = 14.8, $^3J_{9A,10}$ = 5.3, $^3J_{9X,10}$ = 9.9, $^3J_{9X,10}$ = 5.3, $^3J_{9X,10}$ = 9.0), 0.89 t (12-H, $^3J_{HH}$ = 7.3), 1.46 s and 1.58 s (14-H, 16-H). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm (*J*, Hz): 118.12 d.d.t (d) (C^3, $^1J_{CP}$ = 162.8, $^1J_{CH}$ = 169.7, $^3J_{CH}$ = 5.7), 161.07 m (s) (C^4), 124.92 m (d) (C^{4a}, $^3J_{CP}$ = 19.2), 130.46 d (s) (C^5, $^3J_{CH}$ = 7.2), 143.90 m (s) (C^6), 128.05 d (s) (C^7, $^1J_{CH}$ = 158.9), 137.91 m (d) (C^8, $^3J_{CP}$ = 6.6), 147.24 d.d (d) (C^{8a}, $^3J_{CH}$ = 11.3, $^2J_{CP}$ = 11.4), 38.37 t.d.m (s) (C^9, $^1J_{CH}$ = 129.8, $^3J_{CP}$ = 18.6, $^3J_{CH}$ = 6.3), 30.08 t.m (s) (C^{10}), 22.28 t.m (s) (C^{11}, $^1J_{CH}$ = 125.3, $^3J_{CH}$ = $^2J_{CH}$ = 3.2–3.5), 13.80 q.m (s) (C^{12}, $^1J_{CH}$ = 125.0, $^3J_{CH}$ = $^2J_{CH}$ = 3.9–4.1), 35.43 m (s) (C^{13}), 29.96 q.sept (s) (C^{14}, $^1J_{CH}$ = 126.6, $^3J_{CH}$ = 4.6), 37.02 m (s) (C^{15}), 31.16 q.sept (s) (C^{16}, $^1J_{CH}$ = 126.0, $^3J_{CH}$ = 4.6).

4-Butyl-6,8-di-*tert*-butyl-2,5-dichloro-1,2λ^5-benzoxaphosphinine 2-oxide (IV). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 6.31 d (3-H, $^2J_{PH}$ = 24.0), 7.52 br.s and 7.58 br.s (5-H, 7-H), 2.70 m and 2.82 m (1H each, 9-H, *AB* part of *ABX*$_2$ spin system), 1.00 t (12-H, $^3J_{HH}$ = 7.3), 1.37 s (16-H). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm (*J*, Hz): 113.28 d.m (d) (C^3, $^1J_{CP}$ = 157.4, $^1J_{CH}$ = 169.6, $^3J_{CH}$ = 6.0), 157.06 m (s) (C^4), 121.76 m (d) (C^{4a}, $^3J_{CP}$ = 18.3), 121.81 d.d (s) (C^5, $^1J_{CH}$ = 158.0, $^3J_{CH}$ = 7.2), 148.30 m (s) (C^6), 129.94 d.d (s) (C^7, $^1J_{CH}$ = 163.7, $^3J_{CH}$ = 7.2), 124.25 d.d.d (d) (C^8, $^3J_{CP}$ = 8.4, $^2J_{CH}$ = 4.2, $^4J_{CH}$ = 1.3), 144.52 d.d.d.d (d) (C^{8a}, $^3J_{CH}$ = 8.7, 8.7, $^2J_{CP}$ = 9.0), 34.69 t.d.m (s) (C^9, $^3J_{CP}$ = 19.8, $^1J_{CH}$ = 128.0), 30.08 t.m. (s) (C^{10}), 22.28 t.m (s) (C^{11}, $^1J_{CH}$ = 125.3, $^3J_{CH}$ = 3.2–3.5, $^2J_{CH}$ = 3.2–3.6), 13.80 q.m (s) (C^{12}, $^1J_{CH}$ = 125.0, $^2J_{CH}$ = $^3J_{CH}$ = 3.9–4.1). Mass spectrum, *m*/*z*: 402, 404, 406 $[M]^{+\cdot}$. $C_{20}H_{29}Cl_2O_2P$.

4-Butyl-8-*tert*-butyl-6-chloro-2-hydroxy-1,2λ^5-benzoxaphosphinine 2-oxide (V). The glassy residue was treated with water in diethyl ether. The precipitate of compound **V** was filtered off and dried under reduced pressure. Yield 0.88 g (21%, unoptimized), mp 164–166°C. IR spectrum, ν, cm^{-1}: 471, 492, 537, 582, 612, 648, 728, 747, 772, 822, 881, 891, 912, 952, 1001,1016, 1052, 1072, 1110, 1135, 1176, 1206, 1236, 1271, 1319, 1377, 1428, 1462, 1561, 1597, 1667, 2330, 2670, 2725, 2854, 2925, 3469. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 6.15 d (3-H, $^2J_{PH}$ = 18.3),

7.31 br.s (5-H), 7.51 d (7-H, $^4J_{HH}$ = 2.4), 2.62 br.t (9-H, $^3J_{HH}$ = 7.6), 1.46 m (10-H), 1.34 m (11-H), 0.89 t (12-H, $^3J_{HH}$ = 7.3), 1.38 s (14-H). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm (*J*, Hz): 114.13 d.d.t (d) (C^3, $^1J_{CP}$ = 171.4, $^1J_{CH}$ = 162.5, $^3J_{CH}$ = 5.6), 151.46 m (s) (C^4), 123.79 d.d.t (d) (C^{4a}, $^3J_{CP}$ = 15.8, $^3J_{CH}$ = 8.3, 3.2–3.5), 123.74 d.d (s) (C^5, $^1J_{CH}$ = 165.3, $^3J_{CH}$ = 5.8), 126.90 d.d (s) (C^6, $^2J_{CH}$ = 4.9–5.0, 4.9–5.0), 127.47 d.d (s) (C^7, $^1J_{CH}$ = 165.2, $^3J_{CH}$ = 5.8), 141.11 d.m (d) (C^8, $^3J_{CP}$ = 5.6), 148.81 d.d.d (d) (C^{8a}, $^3J_{CH}$ = 8.9–9.1, 9.0, $^2J_{CP}$ = 8.1), 33.89 t.d.m (s) (C^9, $^1J_{CH}$ = 127.9, $^3J_{CP}$ = 17.8), 29.77 m (s) (C^{10}), 21.67 m (s) (C^{11}, $^1J_{CH}$ = 127.8), 13.64 q.t (s) (C^{12}, $^1J_{CH}$ = 124.8, $^3J_{CH}$ = 3.9, $^2J_{CH}$ = 3.9). Found, %: C 58.22; H 6.81; P 9.72. $C_{16}H_{22}ClO_3P$. Calculated, %: C 58.45; H 6.70; P 9.44.

4-Butyl-6-*tert*-butyl-8-chloro-2-hydroxy-1,2-λ^5-benzoxaphosphinine 2-oxide (VI) was isolated by recrystallization from hexane of the mixture obtained after partial separation of compound **V**. Yield 0.1 g (2.4%), mp 174–176°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 6.21 d (3-H, $^2J_{PH}$ = 18.0), 7.53 br.s (5-H), 7.47 d (7-H, $^4J_{CH}$ = 2.0), 2.69 br.m (9-H, $^3J_{HH}$ = 7.4), 1.48 m (10-H), 1.37 m (11-H), 0.90 t (12-H, $^3J_{HH}$ = 7.2), 1.28 s (14-H). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm (*J*, Hz): 114.13 d.d.t (d) (C^3, $^1J_{CP}$ = 171.4, $^1J_{CH}$ = 162.5, $^3J_{CH}$ = 5.6), 151.81 m (s) (C^4), 122.39 m (d) (C^{4a}, $^3J_{CP}$ = 17.3), 121.64 d.d (s) (C^5, $^1J_{CH}$ = 158.2, $^3J_{CH}$ = 7.5), 146.14 m (s) (C^6), 127.73 d.d (s) (C^7, $^1J_{CH}$ = 163.7, $^3J_{CH}$ = 8.1), 122.31 d.d (d) (C^8, $^3J_{CP}$ = 7.1, $^2J_{CH}$ = 5.9), 144.59 d.d.d (d) (C^{8a}, $^3J_{CH}$ = 9.0, 9.0, $^2J_{CP}$ = 6.8), 33.66 t.d.m (s) (C^9, $^1J_{CH}$ = 128.0, $^3J_{CP}$ = 17.8), 29.94 t.d.m (s) (C^{10}, $^1J_{CH}$ = 127.0), 21.67 m (s) (C^{11}, $^1J_{CH}$ = 127.8), 13.64 q.m (s) (C^{12}, $^1J_{CH}$ = 124.8, $^3J_{CH}$ = 3.9, $^2J_{CH}$ = 3.9). Found, %: C 58.37; H 7.09; P 9.51. $C_{16}H_{22}ClO_3P$. Calculated, %: C 58.45; H 6.70; P 9.44.

The NMR spectra were recorded on a Bruker CXP-100 (^{31}P) and Bruker Avance-600 instruments (^{1}H, ^{13}C). The IR spectrum was obtained on a Bruker Vector-22 spectrometer from a sample of **V** dispersed in mineral oil.

This study was performed under financial support by the Foundation for Support of the Russian Science and by the President of the Russian Federation (project no. MK-1434.3.06).

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