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SHORT COMMUNICATIONS

Predominant Formation of 4-Butyl-2,5-dichloro-2-oxo-1,2λ^5-benzoxaphosphinine-6-carbonyl Chloride in the Reaction of 2,2,2-Trichloro-1,3,2λ^5-benzodioxaphosphole-5-carbonyl Chloride with Hex-1-yne

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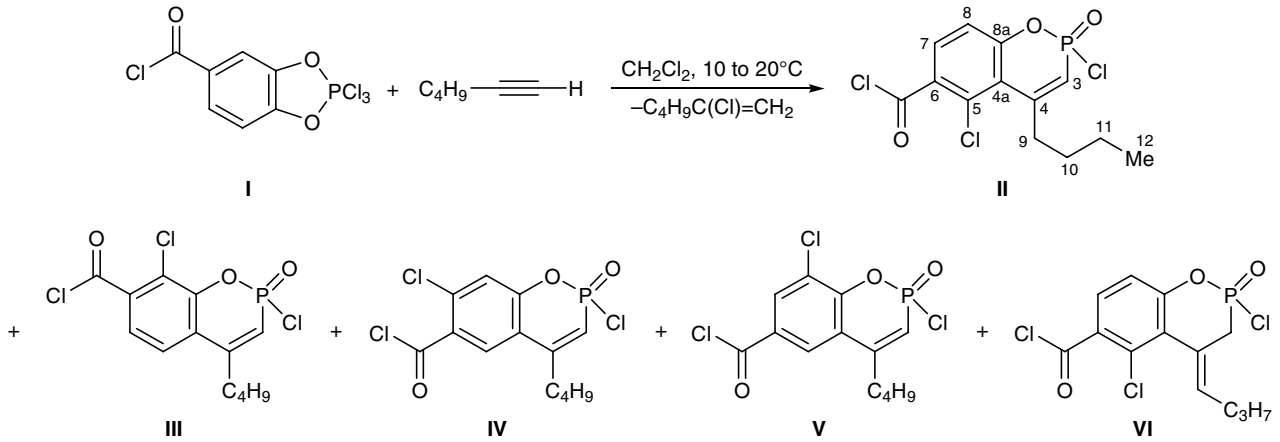
Reactions of aryl- and alkylacetylenes with 2,2,2-trichloro(bromo)-1,3,2λ^5-benzodioxaphosphole and some its derivatives containing a substituent in the benzene ring [1–3] underlie a convenient synthetic approach to 1,2λ^5-benzoxaphosphinines that are phosphorus-containing analogs of widespread natural compounds, coumarins and α-chromenes [4–6]. With a view to examine the effect of substitution in the fused benzene ring on the regioselectivity of reactions with alkylacetylenes, we examined the reaction of 2,2,2-trichloro-1,3,2λ^5-benzodioxaphosphole-5-carbonyl chloride (**I**) with hex-1-yne. Dioxaphosphole **I** was obtained by phosphorylation of naturally occurring protocatechic acid [1]; its molecule contains an electron-acceptor chloroformyl substituent in the *para* position with respect to one oxygen atom in the heteroring. We found that compound **I** reacts with hex-1-yne in a way different from the reaction of 2,2,2-trichloro-1,3,2λ^5-benzodioxaphosphole with the same reagent [3]. Although the products are only 1,2λ^5-benzoxaphosphinine derivatives **II**–**VI**, the process is more complex and is characterized by specific regioselectivity of replacement of the oxygen atom and chlorination of the fused benzene ring. According to the ^{13}C, ^{13}C–{^{1}H}, and ^{1}H NMR data, the major product is 4-butyl-2,5-dichloro-2-oxo-1,2λ^5-benzoxaphosphinine-6-carbonyl chloride (**II**) (>75%). The reaction of dioxaphosphole **I** with phenylacetylene, apart from isomeric 4-phenyl-1,2-benzoxaphosphinines that are analogous to compounds **II** and **V** (ratio 2:1), gave a classical electrophilic addition product, 2-(2-chloro-2-phenylethenyl)-2,2-dichloro-1,3,2λ^5-benzodioxaphosphole [1].

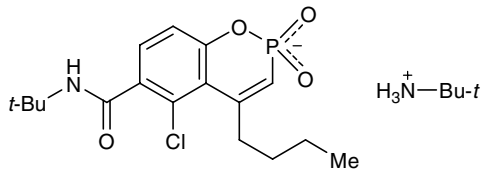
In the ^{1}H NMR spectrum of **II**, protons in the benzene ring (7-H and 8-H) give rise to an *AB* spin system. The ratio of products **III**–**VI** was 2:1:1:2;



I II III IV V VI

they were also identified by NMR spectroscopy. Compounds **III**–**V** showed in the ^{13}C NMR spectrum a doublet signal from C^3 (δ_C 115.62, 114.38, 113.05 ppm; $^1J_{PC}$ = 155.1, 155.0, 154.9 Hz, respectively). The signal from C^8 in the spectra of **III** and **V** appeared as a doublet at δ_C 125.82 ppm ($^3J_{PC}$ = 7.0 Hz) and 124.05 ppm ($^3J_{PC}$ = 8.0 Hz), respectively, indicating formation of 8-chloro-substituted derivatives. The position of the Cl and COCl substituents is confirmed by multiplicity of the C^5 (δ_C 127.11 ppm, d, $^1J_{CH}$ = 167.4 Hz) and C^6 signals (δ_C 124.37 ppm, d, $^1J_{CH}$ = 164.5 Hz) in the spectrum of **III** and of the C^5 (δ_C 127.80 ppm, d.d, $^1J_{CH}$ = 166.8, $^3J_{CH}$ = 6.5 Hz) and C^7 signals (δ_C 134.23 ppm, d.d, $^1J_{CH}$ = 171.9, $^3J_{CH}$ = 7.2 Hz) in the spectrum of **V**. The downfield region of the ^1H NMR spectra of compounds **III** and **V** characteristically contained the following signals, δ, ppm: **III**: 7.68 d (6-H, $^3J_{HH}$ = 8.6 Hz), 7.92 d (5-H, $^3J_{HH}$ = 8.6 Hz), 6.64 d (3-H, $^2J_{PH}$ = 23.1 Hz); **V**: 7.28 d.d (7-H, $^4J_{HH}$ = 2.0, $^5J_{PH}$ = 1.6 Hz), 8.25 d (5-H, $^4J_{HH}$ = 2.0 Hz), 6.43 d (3-H, $^2J_{PH}$ = 23.0 Hz). 4-Butyl-2,7-dichloro-2-oxo-1,2λ^5-benzoxaphosphinine-6-carbonyl chloride (**IV**) was identified by the presence in the ^1H NMR spectrum of signals from 5-H and 8-H at δ 8.39 and 7.40 ppm, respectively. Apart from minor benzoxaphosphinines **III**–**V**, we also succeeded in detecting product **VI** resulting from allyl shift of proton from C^9 to C^3. Compound **VI** was formed when the reaction mixture was heated to 150–160°C. It showed the following signals in the ^1H NMR spectrum, δ, ppm: 7.94 d.d (7-H, $^3J_{HH}$ = 8.8, $^5J_{PH}$ = 1.4 Hz), 7.14 d (8-H, $^3J_{HH}$ = 8.8 Hz), 3.31 m and 3.50 m [PCH_AH_B, *AB* part of *ABX* system, $^2J_{AB}$ = 15.4, $^2J(PH_A)$ = 19.5, $^2J(PH_B)$ = 18.6 Hz]; the C^3 signal appeared in the ^{13}C NMR spectrum as a doublet at δ_C 33.41 ppm ($^1J_{PC}$ = 101.7 Hz).

By treatment of the reaction mixture with *tert*-butylamine and subsequent fractional crystallization from aqueous acetone we isolated ammonium salt **VII**.



VII

We can conclude that benzodioxaphosphole **I** is capable of reacting not only with arylacetylenes but also with hex-1-yne to give 1,2λ^5-benzoxaphosphinine derivatives. The presence of a chloroformyl group in the benzene ring of **I** changes the regioselectivity of the process, so that the major product is compound **II** in which the chlorine atom is located in the *ortho* position, and the chloroformyl group, in the *meta* position with respect to C^{4a}.

Reaction of 2,2,2-trichloro-1,3,2λ^5-benzodioxaphosphole-5-carbonyl chloride (I) with hex-1-yne. A mixture of 4.51 g (0.015 mol) of compound **I**, 5 ml of methylene chloride, and 3.4 ml (2.43 g, 0.03 mol) of hex-1-yne was kept for 12 h at 10–20°C. The solvent and volatile components were removed under reduced pressure (12 mm), and the residue was dried in a vacuum (0.1 mm). It was a glassy material containing benzoxaphosphinines **II**–**VI** which were characterized by spectral data. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 6.54 d (1H, 3-H, $^2J_{PH}$ = 25.0 Hz), 8.0 d.d (1H, 7-H, $^3J_{HH}$ = 8.8, $^5J_{PH}$ = 1.5 Hz), 7.35 d (1H, 8-H, $^3J_{HH}$ = 8.8 Hz), 2.88 and 3.23 (9-H_A, 9-H_B, $^2J_{AB}$ = 15.7, $^3J_{H,A}$ = 6.6, 9.4, $^3J_{H,B}$ = 6.8, 9.4 Hz), 1.51 m (10-H), 1.34 m (11-H, $^3J_{HH}$ = 7.2–7.4, 7.3–7.4 Hz), 0.90 m (12-H, $^3J_{HH}$ = 7.3–7.4 Hz). ^{13}C NMR spectrum of compound **II** ($CDCl_3$), δ_C, ppm [hereinafter, signal multiplicities in the ^{13}C–{^1H} spectrum are given in parentheses): 118.99 d.d.t (d) (C^3, $^1J_{PC}$ = 158.0, $^1J_{CH}$ = 170.6, $^3J_{CH}$ = 6.3 Hz), 157.78 m (s) (C^4), 123.45 m (d) (C^{4a}, $^3J_{PC}$ = 19.5 Hz), 133.55 d.d (d) (C^5, $^3J_{CH}$ = 8.0, $^4J_{PC}$ = 2.0 Hz), 131.43 m (d) (C^6, $^3J_{CH}$ = 10.5, $^4J_{PC}$ = 2.5 Hz), 133.17 d (s) (C^7, $^1J_{CH}$ = 169.5 Hz), 119.05 d.d (d) (C^8, $^3J_{PC}$ = 7.5, $^1J_{CH}$ = 171.3 Hz), 153.28 d.d.d (d) (C^{8a}, $^3J_{CH}$ = 11.3, $^2J_{PC}$ = 10.3, $^2J_{CH}$ = 3.9 Hz), 37.60 t.d.m (d) (C^9, $^1J_{CH}$ = 134.1, $^3J_{PC}$ = 18.4, $^2J_{CH}$ = 3.8–4.4, $^3J_{CH}$ = 3.8–4.4 Hz), 30.73 t.m (s) (C^{10}, $^1J_{CH}$ = 128.2 Hz), 21.96 t.m (s) (C^{11}, $^1J_{CH}$ = 130.7 Hz), 13.43 q.m (s) (C^{12}, $^1J_{CH}$ = 125.1, $^2J_{CH}$ = 3.8, $^3J_{CH}$ = 3.9–4.0 Hz). ^{31}P NMR spectrum (36.48 MHz, CH_2Cl_2), δ_P, ppm: 17.4 d ($^2J_{PH}$ = 25.0 Hz) (**II**); 17.9–18.7 d ($^2J_{PH}$ = 25.0–27.0 Hz) (**III**–**V**); 17.7 d ($^2J_{PH}$ = 23.1 Hz) (**VI**). Found: $[M]^+$ 352. $C_{13}H_{12}Cl_3O_3P$. Calculated: *M* 352 (^{35}Cl).

The glassy material was dissolved in 7 ml of methylene chloride, and a mixture of 3.1 ml of *tert*-butylamine and 3.1 ml of triethylamine was added. After 24 h, the precipitate of ammonium salt was filtered off. The filtrate was washed with an aqueous solution of sodium carbonate (pH 8) and evaporated under reduced pressure (15 mm), the residue was treated with diethyl ether, and the precipitate of *tert*-butylammonium 4-butyl-6-*tert*-butylaminocarbonyl-5-chloro-2-oxo-1,2λ^5-oxaphosphinin-2-olate (**VII**) was filtered off, washed with diethyl ether, and dried under reduced pressure (12 mm). Yield 47%, mp 183–186°C. IR spectrum, ν, cm^{-1}: 461, 542, 575, 614, 652, 722, 803, 821, 848, 900, 937, 1077, 1142, 1166, 1211, 1311,

1536, 1594, 1654, 2533, 2619 v.br, 2724 v.br, 2854, 2924, 3255, 3447. ^{1}H NMR spectrum (600 MHz, DMSO-d_6), δ, ppm: 6.19 d (1H, 3-H, $^2J_{PH}$ = 18.3 Hz), 7.11 d (1H, 7-H, $^3J_{HH}$ = 8.4 Hz), 6.92 d (1H, 8-H, $^3J_{HH}$ = 8.4 Hz), 7.83 s (1H, NH), 8.09 br.s (3H, H_3N^+), 2.79 br.t (2H, 9-H, $^3J_{HH}$ = 7.3 Hz), 1.38 m (2H, 10-H, $^3J_{HH}$ = 7.3–7.8 Hz), 1.27 m (2H, 11-H, $^3J_{HH}$ = 7.3–7.8 Hz), 0.85 t (3H, 12-H, $^3J_{HH}$ = 7.3 Hz). ^{13}C NMR spectrum (150.9 MHz, DMSO-d_6), δ_C, ppm: 128.24 d.d.t (d) (C^3, $^1J_{PC}$ = 166.3, $^1J_{CH}$ = 154.4, $^3J_{CH}$ = 6.0 Hz), 144.63 m (s) (C^4), 124.15 m (d) (C^{4a}, $^3J_{PC}$ = 16.3 Hz), 133.89 d (s) (C^5, $^3J_{CH}$ = 8.7 Hz), 127.42 br.d (s) (C^6, $^3J_{CH}$ = 12.0 Hz), 126.97 d (s) (C^7, $^1J_{CH}$ = 164.0 Hz), 117.83 d.d (d) (C^8, $^3J_{PC}$ = 4.6, $^1J_{CH}$ = 164.3 Hz), 154.80 d.d.d (d) (C^{8a}, $^3J_{CH}$ = 11.2, $^2J_{CH}$ = 3.2, $^2J_{PC}$ = 7.1 Hz), 36.59 d.t.m (d) (C^9, $^3J_{PC}$ = 15.3, $^1J_{CH}$ = 124.7 Hz), 30.74 t.m (s) (C^{10}, $^1J_{CH}$ = 123.2, $^2J_{CH}$ = $^3J_{CH}$ = 3.8–4.0 Hz), 21.63 t.m (s) (C^{11}, $^1J_{CH}$ = 122.3, $^2J_{CH}$ = 3.8–4.0, $^3J_{CH}$ = 3.8–4.0 Hz), 13.52 q.m (s) (C^{12}, $^1J_{CH}$ = 125.7, $^2J_{CH}$ = $^3J_{CH}$ = 4.1 Hz), 50.60 m (s) and 50.67 m (s) (CNH, CN^+H_3), 28.39 q.sept.d (s) (**C**CNH, $^1J_{CH}$ = 126.0, $^3J_{CH}$ = 4.2, 1.8 Hz), 27.02 br.q.sept (s) [**C**CN^+H_3, $^1J_{CH}$ = 126.8, $^3J_{CH}$ = 4.1 Hz). Found, %: C 56.27; H 7.95; N 6.03; P 7.39. $C_{21}H_{34}ClN_2O_4P$. Calculated, %: C 56.69; H 7.65; N 6.30; P 6.97.

The NMR spectra were recorded on Bruker CXP-100 (^{31}P), Bruker MSL-400 (^{13}C), and Bruker Avance-600 (^{1}H) spectrometers. The IR spectrum was measured in mineral oil on a Bruker Vector-22 instrument.

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