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LETTERS TO THE EDITOR

Effect of Electronic Nature of Substituents in Arylacetylene on the Rate of Reaction with 2,2,2-Trichloroareno-1,3,2-dioxaphosphols

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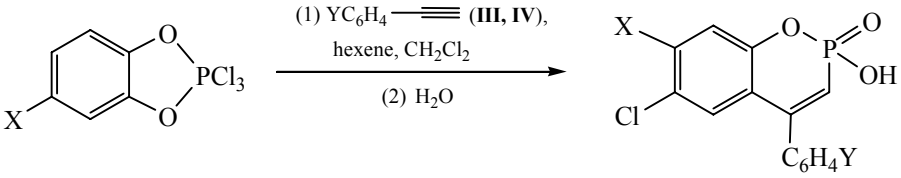
Reaction of 2,2,2-trihaloareno-1,3,2-dioxaphosphols with the terminal acetylenes is a convenient method for the synthesis of benzo-1,2-oxaphosphorine-2-oxide derivatives [1]. Formation of the latter is a multi-step process. So far a number of regularities of influence of the phosphorus center nature on a result of the reaction is known [2]. However, there is no information on the effect of the nature of substituents in arylacetylene on synthetic result as well as on the reaction rate. To estimate the effect of the electronic properties of the substituent in arylacetylene we investigated the reaction of benzodioxaphosphols **I**, **II** with arylacetylenes **III**, **IV**, containing in the *p*-position strong +*M*-donor like a methoxy group, or a strong *M*-acceptor such as nitro group.

Both phosphoranes **I**, **II** react easily with acetylenes **III**, **IV** to produce after hydrolysis of the reaction mixture the benzooxaphosphorine derivatives **V**–**VIII** in high yields. The structure of the isolated compounds was identified by spectroscopic methods (IR, ^{1}H NMR, ^{31}P, ^{13}C). Thus, the introduction of the strong +*M*-donors as well as the strong –*M*-acceptors into arylacetylene does not prevent the formation of benzooxaphosphorine derivatives.

In order to estimate the reaction rate we investigated the competitive reactions of benzodioxaphosphols **I** and **II** with pairs phenylacetylene–compound **III** and phenylacetylene–compound **IV**. The reaction progress was monitored by ^{1}H NMR. It was found that from the first pair 4-methoxyphenylacetylene **III** reacts predominantly (over 75%) and from the second pair, exclusively phenylacetylene. Thus, the rate determining stage of the reaction is very sensitive to the electronic nature of the aryl substituent. The reaction rate increases as the donor nature of the substituent enhances. Apparently, this stage is the donor-acceptor interaction of phosphol as a Lewis acid with arylacetylene as a Lewis base.

The NMR spectra were registered on an Avance-400 spectrometer [400.0 (^{1}H), 162.0 (^{31}P), 100.6 MHz



I, II **V–VIII**

X = H (**I**), Me (**II**); Y = 4-MeO (**III**), 4-NO_2 (**IV**); X = H, Y = 4-MeO (**V**), 4-NO_2 (**VI**); X = Me, Y = 4-MeO (**VII**), 4-NO_2 (**VIII**).

(^{13}C)] in DMSO-d_6 (unless otherwise indicated) relative to internal TMS or HMDS, or external H_3PO_4. The IR spectra were recorded on a Bruker Vector-22 instrument for suspensions in mineral oil. Phosphoranes **I**, **II** were prepared according to [3]. The reaction with arylacetylenes was carried out in CH_2Cl_2 under argon atmosphere followed by hydrolysis under conditions similar to the reaction of compound **I** with phenylacetylene [4].

2-Hydroxy-4-(4-methoxyphenyl)-6-chlorobenzyl-[*e*]-1,2-oxaphosphorine-2-oxide (V). Yield 73%, mp 272°C. IR spectrum, ν, cm^{-1}: 441, 449, 537, 565, 585, 641, 721, 776, 801, 829, 886, 908, 960, 1014, 1112, 1151, 1178, 1221, 1247, 1294, 1337, 1377, 1463, 1510, 1551, 1574, 1606, 1667, 2330, 2359, 2675, 2724, 2854, 2923, 2954, 3435. ^{1}H NMR spectrum (DMSO-d_6:$CDCl_3$ = 1:4), δ_H, ppm (*J*, Hz): 3.58 s (3H, C^{13}H), 6.07 d (1H, C^{3}H, $^2J_{PH}$ 17.8), 6.93 d (2H, C^{11}H, *AA*'-part of *AA*'*XX*'-system), 7.09 d (1H, C^{5}H, $^4J_{HH}$ 2.2), 7.10 d (1H, C^{8}H, $^3J_{HH}$ 8.3), 7.22 m (2H, C^{10}H, *XX*'-part of *AA*'*XX*'-system), 7.26 d. d. d (1H, C^{7}H, $^3J_{HH}$ 8.3, $^4J_{HH}$ 2.2, $^5J_{PH}$ 1.6). ^{13}C–{^{1}H} NMR spectrum, (DMSO-d_6:$CDCl_3$ = 1:4), δ_C, ppm (*J*, Hz): 114.80 d. d (d) (C^3, $^1J_{PC}$ 171.7, $^1J_{HC}$ 163.2), 151.18 m (d) (C^4, $^2J_{PC}$ 1.5), 123.38 d. d. d (d) (C^{4a}, $^3J_{PC}$ 16.1, $^3J_{HC}$ 5.5, $^3J_{HC}$ 7.7), 127.86 d. d (s) (C^5, $^1J_{HC}$ 166.2, $^3J_{HC}$ 5.5), 127.47 d d d (s) (C^6, $^3J_{HC}$ 11.4, $^2J_{HC}$ 4.0, $^2J_{HC}$ 4.0), 129.94 d d (s) (C^7, $^1J_{HC}$ 169.1, $^3J_{HC}$ 5.9), 120.42 d. d (d) (C^8, $^1J_{HC}$ 166.2, $^3J_{PC}$ 7.4), 149.76 d. d. d. d (d) (C^{8a}, $^2J_{PC}$ 7.3, $^3J_{HC}$ 10.2, $^3J_{HC}$ 10.2, $^2J_{HC}$ 4.0), 129.91 d t (d) (C^9, $^3J_{PC}$ 18.7, $^3J_{HC}$ 7.7), 129.26 d. d (s) (C^{10}, $^1J_{HC}$ 159.2, $^2J_{HC}$ 7.7), 113.74 d d (s) (C^{11}, $^1J_{HC}$ 160.3, $^2J_{HC}$ 4.4), 159.77 m (s) (C^{12}), 54.91 q (s) (C^{13}, $^1J_{HC}$ 171.5). ^{31}P NMR spectrum, (DMSO-d_6): δ_P 4.7 ppm (d, $^2J_{PH}$ 17.6 Hz). Found, %: C 54.98; H 4.30; Cl 10.87; P 9.54. $C_{15}H_{12}ClO_4P$. Calculated, %: C 55.83; H 3.75; Cl 10.99; P 9.60.

2-Hydroxy-4-(4-nitrophenyl)-6-chlorobenzo[*e*]-1,2-oxaphosphorine-2-oxide (VI). Yield 92%, mp 321°C (decomp.). IR spectrum, ν, cm^{-1}: 3435, 2346, 2029, 1976, 1959, 1655, 1638, 1616, 1588, 1572, 1537, 1445, 1394, 1343, 1313, 1243, 1197, 1181, 1166, 1119, 1076, 1006, 966, 929, 880, 862, 820, 761, 748, 701, 668, 629, 601, 588, 570, 537, 511, 434. ^{1}H NMR spectrum, δ_H, ppm (*J*, Hz): 6.53 d (1H, C^{3}H, $^2J_{PH}$ 16.4), 6.97 d (1H, C^{5}H, $^4J_{HH}$ 2.6), 7.34 d (1H, C^{8}H, $^3J_{HH}$ 8.7), 7.52 d. d. d (1H, C^{7}H, $^3J_{HH}$ 8.7, $^4J_{HH}$ 2.6, $^5J_{PH}$ 1.4), 7.68 m (2H, C^{10}H, *AA*'-part of *AA*'*XX*'-system), 8.33 m (2H, C^{11}H, *XX*'-part of *AA*'*XX*'-system). ^{13}C–{^{1}H} NMR spectrum, δ_C, ppm (*J*, Hz): 119.70 d. d (d) (C^3, $^1J_{PC}$ 167.6, $^1J_{HC}$ 164.7), 148.80 m (s) (C^4), 123.38 d. d. d. (d) (C^{4a}, $^3J_{PC}$ 16.5, $^3J_{HC}$ 8.1, $^3J_{HC}$ 8.0), 127.68 d. d (s) (C^5, $^1J_{HC}$ 165.8, $^3J_{HC}$ 5.1), 127.68 d. d. d (s) (C^6, $^3J_{HC}$ 11.4, $^2J_{HC}$ 3.6, $^2J_{HC}$ 3.6), 131.29 d. d (s) (C^7, $^1J_{HC}$ 170.2, $^3J_{HC}$ 5.9), 121.82 d. d (d) (C^8, $^1J_{HC}$ 168.0, $^3J_{PC}$ 6.6), 150.49 d. d. d. d (d) (C^{8a}, $^2J_{PC}$ 7.3, $^3J_{HC}$ 8.4, $^3J_{HC}$ 8.4, $^2J_{HC}$ 3.7), 144.71 d. t. d (d) (C^9, $^3J_{PC}$ 18.7, $^3J_{HC}$ 7.3, $^3J_{HC}$ 7.3), 124.38 d. d (s) (C^{10}, $^1J_{HC}$ 170.6, $^2J_{HC}$ 4.0), 130.36 d. d (s) (C^{11}, $^1J_{HC}$ 166.5, $^2J_{HC}$ 6.6), 148.16 m (s) (C^{12}, $^3J_{HC}$ 9.2). ^{31}P NMR spectrum: δ_P 3.3 ppm (d, $^2J_{PH}$ 16.7 Hz). Found, %: C 48.20; H 2.93; Cl 11.40; N 4.28; P 8.97. $C_{14}H_9ClNO_5P$. Calculated, %: C 49.80; H 2.69; Cl 11.40; N 4.15; P 9.17.

2-Hydroxy-7-methyl-4-(4-methoxyphenyl)-6-chlorobenzo[*e*]-1,2-oxaphosphorine-2-oxide (VII). Yield 84%, mp 286°C. IR spectrum, ν, cm^{-1}: 2550 br, 2290 br (POH), 1611, 1595, 1539, 1510, 1483, 1460, 1376, 1337, 1302, 1294, 1248, 1179, 1166, 1128, 1033, 1014, 922, 890, 883, 860, 853, 820, 801, 782, 748, 739, 722, 666, 631, 584, 553, 535, 521, 484, 463, 444, 415. ^{1}H NMR spectrum, δ_H, ppm (*J*, Hz): 2.36 s (3H, CH_3), 3.83 s (3H, CH_3O), 6.22 d (1H, C^{3}H, $^2J_{PH}$ 17.8), 7.08 s (H^5), 7.32 br. s (H^8), 7.06 m (2H, C^{11}H, *AA*'-part of *AA*'*XX*'-system, $^3J_{HH}$ 8.8), 7.32 m (2H, C^{10}H, *XX*'-part of *AA*'*XX*'-system, $^3J_{HH}$ 8.8). ^{13}C–{^{1}H} NMR spectrum, δ_C, ppm (*J*, Hz): 19.91 q. d (s) (CH_3, $^1J_{HC}$ 128.6, $^3J_{HC}$ 4.6), 55.74 q (s) (CH_3O, $^1J_{HC}$ 144.5), 115.76 d. d (d) (C^3, $^1J_{PC}$ 169.4, $^1J_{HC}$ 163.5), 150.78 m (d) (C^4, $^2J_{PC}$ 1.5), 122.04 d. d. d (d) (C^{4a}, $^3J_{PC}$ 16.5, $^3J_{HC}$ 8.8, $^3J_{HC}$ 5.8), 128.30 d (s) (C^5, $^1J_{HC}$ 164.6), 127.82 d. q (s) (C^6, $^2J_{HC}$ 5.6, $^3J_{HC}$ 5.0), 139.22 d. q (s) (C^7, $^3J_{HC}$ 6.3, $^2J_{HC}$ 6.3), 122.23 d. d. q (d) (C^8, $^1J_{HC}$ 164.3, $^3J_{PC}$ 7.0, $^3J_{HC}$ 5.6), 150.31 d. d. d (d) (C^{8a}, $^2J_{PC}$ 7.0, $^3J_{HC}$ 7.0, $^2J_{HC}$ 3.4), 130.53 d. t. d (d) (C^9, $^3J_{PC}$ 18.7, $^3J_{HC}$ 7.8, $^3J_{HC}$ 6.4), 130.18 d. d (s) (C^{10}, $^1J_{HC}$ 159.5, $^2J_{HC}$ 7.4), 114.70 d. d (s) (C^{11}, $^1J_{HC}$ 160.5, $^2J_{HC}$ 4.7), 160.35 m (s) (C^{12}). ^{31}P NMR spectrum: δ_P 3.0 ppm (d, $^2J_{PH}$ 17.5 Hz). Found, %: C 56.79; H 4.87; Cl 10.34; P 9.05. $C_{16}H_{14}ClO_4P$. Calculated, %: C 57.06; H 4.19; Cl 10.53; P 9.20.

2-Hydroxy-7-methyl-4-(4-nitrophenyl)-6-chlorobenzo[*e*]-1,2-oxaphosphorine-2-oxide (VIII). Yield 90%, mp 324°C (decomp.). IR spectrum, ν, cm^{-1}: 2500–2604 br. s, 2306 br (POH), 1602, 1587, 1516, 1484, 1462, 1376, 1353, 1339, 1312, 1259, 1249, 1190, 1168, 1130, 1109, 1038, 1015, 926, 890, 869, 854, 809, 752, 734, 700, 612, 565, 530, 524, 464, 438. ^{1}H NMR spectrum, δ_H, ppm (*J*, Hz): 2.35 s (3H, CH_3),

6.4 d (1H, C^3H, $^2J_{PH}$ 16.6), 6.94 s (H^5), 7.33 br. s (H^8), 7.66 m (2H, $C^{10}H$, *AA'*-part of *AA'XX'*-system, $^1J_{HH}$ 7.6), 8.32 m (2H, $C^{11}H$, *XX'*-part of *AA'XX'*-system, $^3J_{HH}$ 7.6). $^{13}C–\{^1H\}$ NMR spectrum, δ_C, ppm (*J*, Hz): 19.59 q. d (s) (CH_3, $^1J_{HC}$ 128.7, $^3J_{HC}$ 4.2), 118.15 d. d (d) (C^3, $^1J_{PC}$ 168.0, $^1J_{HC}$ 164.6), 148.57 m (br. s) (C^4), 120.82 m (d) (C^{4a}, $^3J_{PC}$ 16.5), 127.54 d (s) (C^5, $^1J_{HC}$ 164.3), 127.67 d. q (s) (C^6, $^3J_{HC}$ 5.2, $^3J_{HC}$ 4.7), 139.34 d. q (s) (C^7, $^2J_{HC}$ 6.2, $^3J_{HC}$ 6.2), 121.96 d. d. q (d) (C^8, $^1J_{HC}$ 164.7, $^3J_{PC}$ 6.6, $^3J_{HC}$ 3.4), 149.87 d. d. d (d) (C^{8a}, $^2J_{PC}$ 7.0, $^3J_{HC}$ 9.6, $^2J_{HC}$ 3.8), 144.45 d. t (d) (C^9, $^3J_{PC}$ 18.7, $^3J_{HC}$ 7.5), 124.05 d. d (s) (C^{10}, $^1J_{HC}$ 170.2, $^2J_{HC}$ 4.4), 129.98 d. d (s) (C^{11}, $^1J_{HC}$ 166.8, $^2J_{HC}$ 6.8), 147.83 t. t (s) (C^{12}, $^3J_{HC}$ 9.5, $^2J_{HC}$ 3.5). ^{31}P NMR spectrum: δ_P 2.5 ppm (d, $^2J_{PH}$ 15.6 Hz). Found, %: C 50.95; H 3.67; Cl 9.87; N 4.01; P 9.07. $C_{15}H_{11}ClNO_5P$. Calculated, %: C 51.23; H 3.15; Cl 10.08; N 3.98; P 8.81.

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