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SHORT COMMUNICATIONS

Reaction of 2',2',2',2'',2'',2''-Hexabromo-1,4-di(benzo-1,3,2-dioxaphosphol-5-yl)benzene with Phenylacetyleneom

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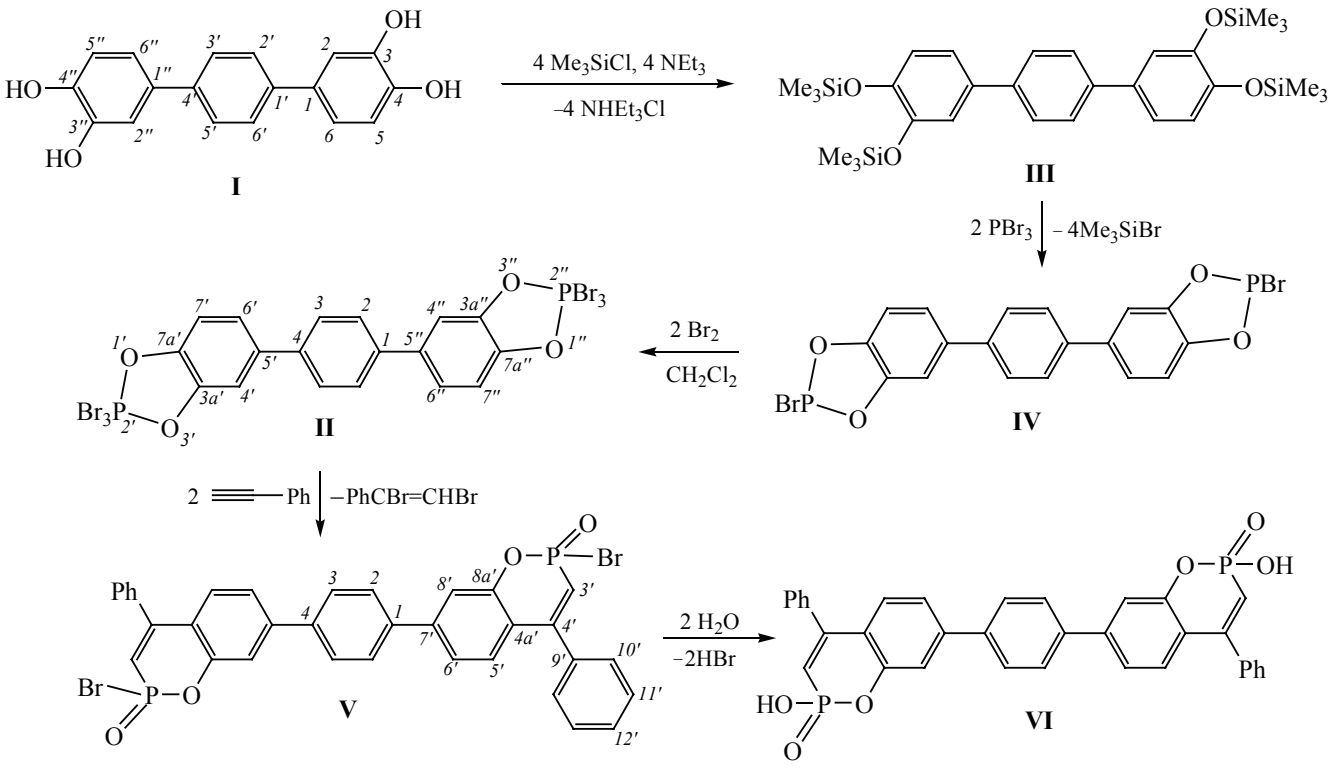
Terphenyl (diphenylbenzene) derivatives are widely used in various fields of physics and chemistry [1–4], biology, and medicine [5, 6]. The derivatives of *m*-terphenyl are widely spread as spatially bulky ligands for the efficien stabilization of organic compounds of the elements of the main groups and of transition metals in the low coordination states [7–9]. *m*-Isomers of terphenyl are used sometimes for the stabilization of compounds with multiple bonds between phosphorus and elements [10].

The reaction of 2,2,2-trihaloareno-1,3,2-dioxaphosphols with acetylenes leads to the formation of areno[*e*]-1,2-oxaphosphorines [11, 12], that attract growing interest because of their possible applications in various fields of chemistry and medicine [13]. It was previously established that the halogenation of the arene fragment occurs the most selectively in the reactions of 2,2,2-tribromoben-



zo-1,3,2-dioxaphosphols with terminal acetylenes [14]. In this study we carried out for the first time the phosphorylation of the *p*-terphenyl derivative, 3,4,3",4"-tetrahydroxy-1,1':4',1"-terphenyl (**I**) with PBr_3 followed by the bromination and the reaction was investigated of the obtained bis(phosphorane) **II** with phenylacetylene. To improve the selectivity of the phosphorylation compound **I** was first converted into tetrakis(trimethylsilyl) ether **III** by treating with trimethylchlorosilane and triethylamine. On adding compound **III** to excess PBr_3 2',2"-dibromo-1,4-di(benzo-1,3,2-λ^3-dioxaphosphol-5-yl)benzene (**IV**) formed quantitatively, that was characterized by a singlet in the ^{31}P NMR spectrum at δ 198 ppm. The Me_3SiBr formed at this stage and excess PBr_3 are easily removed in a vacuum.

The bromination of diphosphol **IV** with bromine was carried out in CH_2Cl_2 solution (–10...–15°C). As a result we obtained 2',2',2',2",2",2"-hexabromo-1,4-di(benzo-1,3,2-λ^5-dioxaphosphol-5-yl)benzene **(II),** which due to its instability against hydrolysis was brought into the reaction with phenylacetylene without further purification. The reaction afforded a single product, 2',2"-dibromo-2',2"-dioxo-4',4"-diphenyl-1,4-di(benzo[*e*]-1,2-oxaphosphorin-7-yl)-benzene **(V)** in the form of two diastereomers in approximately equal ratio. Their appearance is due to the presence in the molecule of two asymmetrical phosphorus atoms.

The high selectivity should be stressed of the process of the *ipso*-substitution of the oxygen atoms in both dioxaphosphol fragments in the *para*-position to the 1,4-phenylene substituents. No bromine is introduced in the annulated phenylene fragment of diphosphorine **V** in contrast to the reactions of the unsubstituted benzodioxaphosphols [15]. After the hydrolysis 2',2"-dihydroxy-2',2"-dioxo-4',4"-diphenyl-1,4-di(benzo[*e*]-1,2-oxaphosphorin-7-yl) benzene (**VI**) was isolated whose structure was established by spectral methods.

2',2"-Dihydroxy-2',2"-dioxo-4',4"-diphenyl-1,4-di(benzo[*e*]-1,2-oxaphosphorin-7-yl)benzene (VI). To 11.4 ml (120 mmol) pf phosphorus tribromide was added dropwise under dry argon atmosphere while stirring a solution of 2.77 g (4.8 mmol) of silyl ether **III** [16] in 15 ml of benzene. After 24 h benzene and volatile products were distilled off from the reaction mixture at the atmospheric pressure and then in a vacuum (12 mm Hg) excess PBr_3 was removed. As a residue a light-yellow thick oily substance was obtained, compound **IV**. ^{31}P NMR spectrum (CH_2Cl_2): δ 198.3 ppm

To a slurry of compound **IV** in 30 ml of CH_2Cl_2 was added dropwise at vigorous stirring a solution of 0.66 ml (13 mmol) of bromine in 5 ml of CH_2Cl_2 (–40°C). The reaction mixture was stirred gradually worming to the room temperature thus obtaining the solution of compound **II**.

To a solution of diphosphol **II** was added dropwise at stirring a solution of 2.6 ml (24 mmol) of phenylacetylene in 5 ml of CH_2Cl_2 (–10 × 0°C). Therewith compound **V** was obtained. ^{31}P-{^1H} NMR spectrum (^{31}P) (CH_2Cl_2), δ, ppm: 9.4 s , 9.3 br.d ($^2J_{PC^3H}$ 26.4 Hz).

From the solution of compound **V** the solvent and volatile products were removed in a vacuum, the residue was kept in air for 4 h, washed with hexane, dissolved in acetone, and precipitated by ethanol. The formed light-brown precipitate was filtered off, washed with a little acetone and ether, and dried in a vacuum. After several crystallizations from ethanol we isolated 1.77 g (63%) of compound **VI**, mp >350°C. IR spectrum, 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. ^1H NMR spectrum (DMSO-d_6), δ, ppm: 6.28 d ($H^{3'}$, $^2J_{PCH}$ 17.5 Hz), 7.19 d ($H^{5'}$, $^3J_{HCCH}$ 8.2 Hz), 7.66 d ($H^{8'}$, $^4J_{HCCCH}$ 1.8 Hz), 7.55 d.d ($H^{6'}$, $^3J_{HCCH}$ 8.2, $^4J_{HCCCH}$ 1.8 Hz), 7.88 s ($H^{2,3,5,6}$), 7.40–7.54 m ($C^{4'}$Ph). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 115.88 d.d (d) ($C^{3'}$, $^1J_{PC}$ 169.8, $^1J_{HC}$ 165.1 Hz), 151.65 m (s) ($C^{4'}$), 121.29 m (d) ($C^{4a'}$, $^3J_{PCCC}$ 16.0 Hz), 129.26 d (s) ($C^{5'}$, $^1J_{PC}$ 161.4 Hz), 121.50 d.d (s) ($C^{6'}$, $^1J_{HC}$ 162.4, $^3J_{HCCC}$ 6.8 Hz), 141.98 m (s) ($C^{7'}$), 117.02 br.d.d.d (d) ($C^{8'}$, $^1J_{HC}$ 162.4, $^3J_{HCCC}$ 6.8, $^3J_{POCC}$ 5.6 Hz), 151.97 m (d) ($C^{8a'}$, $^2J_{POC}$ 5.9 Hz), 138.57 m (d) ($C^{9'}$, $^3J_{PCCC}$ 18.7 Hz), 128.47 br.d.d.d (s) ($C^{10'}$, $^1J_{HC}$ 160.7, $^3J_{HCCC}$ 6.6, $^3J_{HCCC}$ 5.5 Hz), 128.87 d.d (s) ($C^{11'}$, $^1J_{HC}$ 162.0, $^3J_{HCCC}$ 7.5 Hz), 129.04 d.t (s) ($C^{12'}$, $^1J_{HC}$ 161.2, $^3J_{HCCC}$ 7.5 Hz), 138.17 m (s) ($C^{13'}$, $^3J_{HCCC}$ 4.5, $^3J_{HCCC}$ 3.5 Hz), 127.57 br.d (s) ($C^{14',15'}$, $^1J_{HC}$ 160.3 Hz). ^{31}P NMR spectrum (DMSO), δ, ppm: 5.53 br.d ($^2J_{PCH}$ 17.5 Hz). Found, %: C 68.80; H 4.23; P 10.64. $C_{34}H_{24}O_6P_2$. Calculated, %: C 69.16; H 4.10; P 10.49.

Compounds **I** and **III** were obtained by procedures [16, 17]. ^1H, ^{13}C, ^{13}C-{^1H}, ^{31}P, ^{31}P-{^1H} NMR spectra were registered on a spectrometer Bruker Avance-400 [400 (^1H), 162.0 (^{31}P), 100.6 MHz (^{13}C)] using as internal reference the signals of the residual protons or carbon atoms of the solvent, and as external reference, H_3PO_4. IR spectrum was recorded on an instrument Bruker Vector-22 from mull in mineral oil.

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REFERENCES,

1. Liu, J.-K., *Chem. Rev.,* 2006, vol. 106, no. 6, p. 2209.
2. Zhou, D., Chen, Y., Chen, L., Li, F., and Yao, K., *Synth. Met.,* 2010, vol. 160, p. 892.
3. Luo, Z., Shi, H., Zhu, H., Song, G., and Liu, Y., *Dyes and Pigments.,* 2011, vol. 92, no. 1, p. 596.
4. Shi, Z., Zhang, X., Yang, G., Su, Z., and Cui, Z., *Tetrahedron.,* 2011, vol. 67, p. 22, p. 4110.
5. Li, T., Yang, Y., Cheng, C., Tiwari, A.K., Sodani, K., Zhao, Y., Abraham, I., and Chen, Z.-S., *Bioorg. Med. Chem. Lett.,* 2012, vol. 22, p. 7268.
6. Kikuchi, H., Matsuo, Y., Katou, Y., Kubohara, Y., and Oshima, Y., *Tetrahedron*, 2012, vol. 68, p. 8884.
7. Ni, C. and Power, P.P., *Struct. Bond.,* 2010, vol. 136, p. 59.
8. Twamley, B., Haubrich, S.T., and Power, P.P., *Adv. Organometal, Chem.,* 1999, vol. 44, p. 1.
9. Clyburne, J.A.C. and McMullen, N., *Coord. Chem. Rev.,* 2000, 210, p. 73.
10. Partyka, D.V., Washington, M.P., Updegraff, J.B., Woloszynek, R.A., and Protasiewicz, J.D., *Angew. Chem*., 2008, vol. 47, p. 7489.
11. Mironov, V.F., Konovalov, A.I., Litvinov, I.A., Gubaidullin, A.T., Petrov, R.R., Shtyrlina, A.A., Zyablikova, T.A., Musin, R.Z., Azancheev, N.M., Il'yasov, and A.V., *Zh. Obshch. Khim.,* 1998, vol. 68, p. 1482.
12. Nemtarev, A.V., Varaksina, E.N., Mironov, V.F., Musin, R.Z., and Konovalov, A.I., *Mendeleev Commun.,* 2006, vol. 16, no. 2, p. 98.
13. Li, X., Zhang, D., Pang, H., Shen, F., Fu, H., Jiang, Y., and Zhao, Y., *Org. Lett.,* 2005, vol. 7, no. 22, p. 4919.
14. Mironov, V.F. and Nemtarev, A.V., *Obzorn. Zh. Khim.,* 2011, vol. 1, p. 29.
15. Mironov, V.F., Zyablikova, T.A., Konovalova, I.V., Khanipova, M.G., Petrov, R.R., and Musin, R.A., *Zh. Obshch. Khim.,* 1997, vol. 67, p. 691.
16. Joulie, L.F., Schatz, E., Ward, M.D., Weber, F., and Yellowlees, L.J., *J. Chem. Soc., Dalton, Trans.,* 1994, no. 6, p. 799.
17. Pierce, A.E., *Silylation of Organic Compounds*, Rockford: Pierce Chemical Co., 1968, p. 72.