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LETTERS TO THE EDITOR

Reaction of Phenylacetylene with the *at* Complex on the Basis of Trichloro(phenylenedioxy)phosphorane and Pyridine

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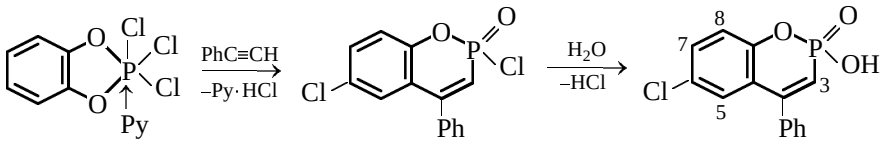
It is known that trichloro(phenylenedioxy)phosphorane (**I**) reacts with arylacetylenes unlike PCl_5 to give 2,6-dichlorobenzo[*e*][1,2]oxaphosphinine 2-oxide as a result of multistage transformations involving an extremely easy formation of the P–C bond and the phosphoryl group, as well as *ipso* substitution of the oxygen atom and regioselective chlorination of the aromatic ring in the *para* position with respect to the endocyclic oxygen atom of the phosphinine heteroring [1].

Proceeding with these studies, in the present work we showed for the first time that the so-called *at* complexes, six-coordinate phosphorus derivatives, can also react with arylacetylenes. For example, a crystalline complex of phosphorane **I** with pyridine [2], which has the structure of phosphorate **II** (δ_P –129.7 and –137.1 ppm, CH_2Cl_2) readily reacts with phenylacetylene to give chlorophosphinine **III** in high yield (δ_P 16.1 ppm, $^2J_{PCH}$ 24.2 Hz, CH_2Cl_2). The reaction involves dissolution of *at* complex **II** and precipitation of pyridine hydrochloride. The latter was separated and identified by spectral methods.



II **III** **IV**

The formation of pyridine hydrochloride points to chlorination of the aromatic fragment. The position of the chlorine atom in the benzene ring was established by comparison of the ^1H and ^{13}C NMR spectra of phosphonic acid **IV** obtained by hydrolysis with the sample of compound **IV** we prepared previously [1].

Note that use of the *at* complex of trichloro(phenylenedioxy)phosphorane with pyridine (complex **II**) in the reaction with phenylacetylene is preferred over use of a double excess of the latter, because in this case there is no need in purification of the reaction product from 1-chloro-1-phenylethylene formed by HCl reaction with the acetylene.

6-Chloro-2-hydroxybenzo[*e*][1,2]oxaphosphinine 2-oxide (IV). Pyridine, 0.99 ml, in 5 ml of CH_2Cl_2 was added with stirring at –20°C under argon to a solution of 3.0 g of phosphorane **I** in 10 ml of CH_2Cl_2. Phenylacetylene, 1.35 ml, was added at –20°C to the resulting precipitate of *at* complex **III**, and the reaction mixture was allowed to warm to 20°C for 1–1.5 h. Therewith, the complex completely dissolved and course crystals of pyridine hydrochloride formed within 5–8 days. The crystals were filtered off, the solvent was removed in a vacuum, the residue was extracted with benzene, and the benzene extract was evaporated. The light yellow glassy residue was dissolved in dioxane and treated with water to isolate 2.86 g (80%) of phosphorine **IV**, mp 258–260°C. ^1H NMR spectrum (250 MHz, DMSO-d_6), δ, ppm (*J*, Hz): 6.36 d (H^3, $^2J_{PCH}$ 17.3), 7.02 d (H^5, $^4J_{HCCCH}$ 2.6), 7.49 d.d.d (H^7, $^3J_{HCCH}$ 8.8, $^4J_{HCCCH}$ 2.6, $^5J_{HCCCCH}$ 1.6), 7.33 d (H^8, $^3J_{HCCH}$ 8.8), 7.52 m and 7.39 m (C_6H_5). For the ^{13}C NMR spectrum, see [1]. Found,

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%: C 57.44; H 3.71; P 10.45. $C_{14}H_{10}ClO_3P$. Calculated, %: C 57.46; H 3.44; P 10.58.

The ^1H, ^{31}P, and ^{13}C NMR spectra were recorded on Bruker WM-250 (250 MHz) and Bruker MSL-400 spectrometers (162.0 and 100.6 MHz, respectively).

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