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CHEMISTRY

Regiochemistry of the Reaction of 3,6-Bis(*tert*-butyl)-1,2-benzoquinone with Phosphorus Trichloride in the Presence of Arylacetylene

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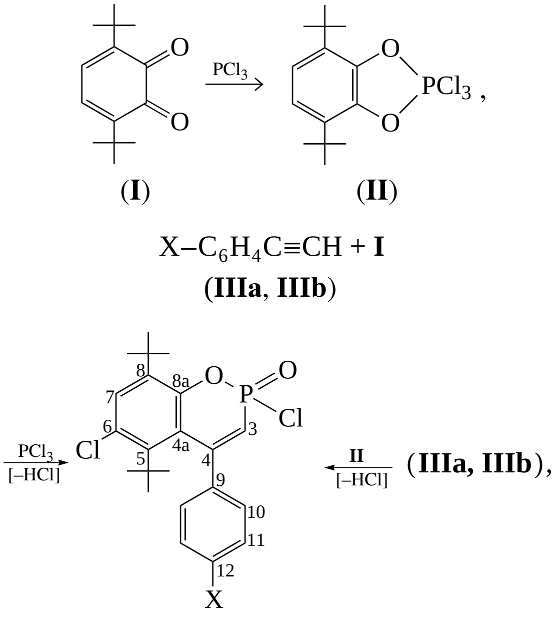
The reaction of phosphorus pentachloride with arylacetylenes followed by hydrolysis of the initially formed phosphonium products is considered as an important method for the synthesis of derivatives of unsaturated phosphonium acids which can be used as initial compounds to prepare various types of new promising biologically active organophosphorus products [1]. The replacement of two chlorine atoms in phosphorus pentachloride by the phenylenedioxy fragment results unexpectedly in 2,6-dichloro-2-oxobenzo[*e*]-1,2-oxaphosphorines, which are products of multistep transformations including easy formation of the P–C bond and the phosphoryl group, *ipso*-substitution of the oxygen atom, and regioselective chlorination of the aromatic ring in the *para*-position relative to endocyclic oxygen of the phosphorine heterocycle [2–4]. A similar synthetic outcome can be attained in the phenanthrenequinone–phosphorus trichloride–arylacetylene ternary system, in which isolation of the intermediate P^V compound is difficult [5].

Herein, we show for the first time that the reaction of sterically hindered 3,6-bis(*tert*-butyl)-1,2-benzoquionone (**I**) with phosphorus trichloride in the presence of arylacetylenes has a number of specific features. First, it should be noted that in the absence of arylacetylene, the reaction of quinone (**I**) with phosphorus trichloride results in the formation of a P^V derivative, 4,7-bis(*tert*-butyl)benzo[*d*]-1,3,2-dioxaphosphole (**II**), which is responsible for a high-field signal with δ_P –27 ppm in the ^{31}P NMR spectrum. Upon the addition of phosphorus trichloride to a mixture of quinone (**I**) with arylacetylene (**IIIa**, **IIIb**), as well as upon the addition of arylacetylene **IIIa** or **IIIb** to benzophosphole **II**, phosphonate products are formed almost quantitatively under mild conditions (10°C, CH_2Cl_2). After keeping *in vacuo* (120°C, 0.1 mmHg), these products represent slightly yellow glasses, which are responsible for a doublet with δ_P 16–18 ppm ($^2J_{PCH}$ 26.5–27.5 Hz) in the ^{31}P NMR spectrum. A similar doublet is present in the ^1H NMR spectra ($CDCl_3$, δ 6.33–6.38 ppm, $^2J_{PCH}$ 26.5–27.5 Hz). Taking account of the data of the ^1H and ^{31}P NMR spectra and the results of a ^{13}C NMR study (see below), the compounds synthesized were identified as 4-aryl-5,8-bis(*tert*-butyl)-6-chlorobenzo[*e*]-1,2-oxaphosphines (**IVa**, **IVb**).



(**I**) (**II**)

$X–C_6H_4C≡CH$ + **I**

(**IIIa**, **IIIb**)

(**IIIa, IIIb**),

(**IVa**, **IVb**)

X = H (**IIa**), 4-CH_3 (**IIb**).

Scheme 1.

It was shown by high-resolution mass spectrometry for compound **IVa** that the process is accompanied by the introduction of a chlorine atom into the *ortho*-phenylene substituent; the spectrum contains a molecular ion peak at 422, which corresponds to the calculated value. The structure of compounds **IV** and the position of the chlorine atom in the aromatic ring were determined by ^{13}C NMR spectroscopy. The spectra exhibit four (for compound **IVb**) or five (for compound **IVa**)

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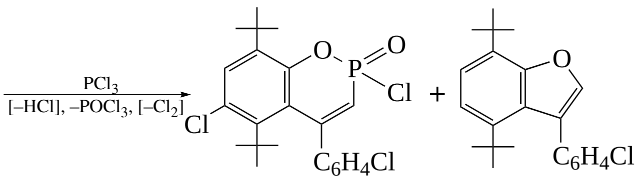
groups of low-field signals for carbon atoms attached to protons and eight (for compound **IVb**) or seven (for compound **IVa**) groups of low-field signals for carbon atoms forming no C–H bonds; this confirms the fact of chlorine introduction into the phenylene substituent. The multiplicity of the C-8a and C-4a signals (**IVa**: 147.73 (ddd, C-8a, $^2J_{POC}$ 11.7 Hz, $^3J_{HCCC}$ 11.2 Hz, $^4J_{HCPOC}$ 1.0 Hz), 125.98 (dd, C-4a, $^3J_{PCCC}$ 20.2 Hz, $^3J_{HCCC}$ 8.1 Hz, $^4J_{HCCCC}$ 0.8 Hz); **IVb**: 147.47 (ddd, C-8a, $^2J_{POC}$ 11.3 Hz, $^3J_{HCCC}$ 10.2 Hz, $^4J_{HCPOC}$ 1.0 Hz), 126.13 (ddd, C-4a, $^3J_{PCCC}$ 20.2 Hz, $^3J_{HCCC}$ 8.1 Hz, $^4J_{HCCCC}$ 1.1 Hz)) points to the formation of a cyclic structure and to the presence of chlorine at C-6. The signal for the C-3 atom shows itself in the typical high-field region (δ_C 113.58–114.39 ppm) as a doublet of doublets with rather high $^1J_{PC}$ (166.2–166.6 Hz) and $^1J_{HC}$ (171.4–172.1 Hz) constants; conversely, the signal of C-4 occurs in low fields (δ_C 159.76–159.87 ppm) as a multiplet ($^2J_{PCC}$ 2.2–2.3 Hz).

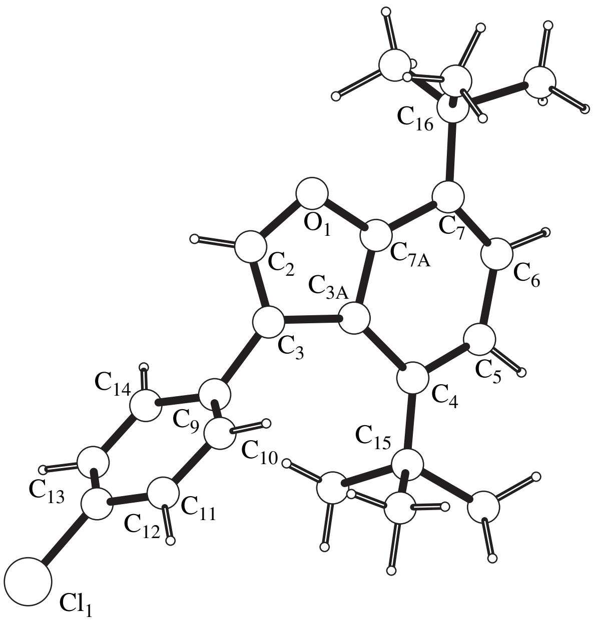
Unlike arylacetylenes **IIIa** and **IIIb**, *para*-chlorophenylacetylene **IIIc** reacts with quinone **I** and phosphorus trichloride less ambiguously than with phosphole **II**. This gives benzophosphorine **IVc** as either the only (with phosphorane **II**) or the major (~62%) reaction product (after removal of CH_2Cl_2 and styrenes at 130°C (0.1 mmHg)). The spectroscopic characteristics of **IVc** (δ_P 17.9 ppm (d, $^2J_{PCH}$ 27.2 Hz), δ_H 6.36 ppm (d, $^2J_{PCH}$ 27.2 Hz)) are close to those for compounds **IVa** and **IVb**. The reaction carried out in a quinone **I**–phosphorus trichloride–acetylene **IIIc** ternary system gave phosphorus oxochloride and a phosphorus-free organic compound, 4,7-bis(*tert*-butyl)-3-*para*-chlorophenylbenzo[*d*]furan (**Vc**), in addition to benzophosphorine **IVc**.

$$\underset{(\mathbf{IIIc})}{Cl{-}C_6H_4C{\equiv}CH} + \mathbf{I}$$



(**IVc**) (**Vc**)

Scheme 2.

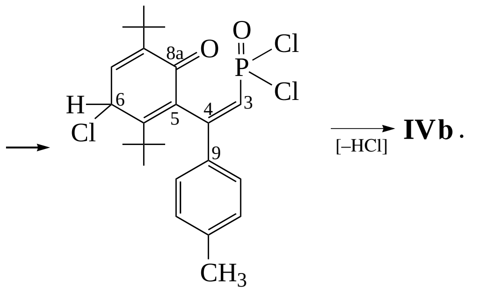


Structure of the molecule of **Vc** in the crystal.

The structure of the isolated crystalline benzofuran (**Vc**) was established by single crystal X-ray diffraction. In the monoclinic crystal of **Vc**, the asymmetric part of the unit cell contains two molecules with nearly the same conformation. The figure shows the geometry of one of the crystallographically independent molecules. The benzofuran fragment is planar to within the experimental error. The key atoms of the *tert*-butyl groups, C(15) and C(16), and of the *para*-chlorophenyl substituent, C(9), are also located in the heterocycle plane. The presence of two bulky substituents in the 3- and 4-positions induces noticeable distortions of the exocyclic bond angles at C(3) (C(3a)C(3)C(9), av. 132.5°) and C(4) (C(3a)C(4)C(15), av. 128.5°) and substantial elongation of the C(3)–C(3a) bond (av., 1.585 Å). The steric hindrance of the bulky substituents stipulates an orthogonal conformation of the *para*-chlorophenyl group; the dihedral angles between the substituent plane and the plane of the benzofuran fragment are 85.4° (mean). Short intramolecular contacts are found between the protons of the methyl groups of the substituent at C(4) and the atoms of the *para*-chlorophenyl substituent in the range of 2.60–2.90 Å. Short contacts between the *tert*-butyl-group protons at C(7) and the O(1) atom conforming to the criterion of the C–H··O hydrogen bond occur in the opposite fragment of the molecule. The formation of compound **Vc** along with the evolution of phosphorus oxochloride is yet another new pathway in these reactions.

Study of the reaction of *para*-methylacetylene with quinone (**I**) and phosphorus trichloride by dynamic ^{31}P NMR spectroscopy showed that initially, this gives a compound responsible for a signal located in a lower field than the signal of phosphorine (**IVb**) [δ_P 30.4 ppm (d, $^2J_{PCH}$ 31.3 Hz)]. Even on heating to 40°C, this signal is gradually transformed into the signal of the final reaction product, benzophosphorine (**IVb**) (δ_P 17.9 ppm). The structure of this intermediate reaction product was elucidated using ^{13}C NMR spectroscopy. Unlike the spectrum of **IVb**, the spectrum of this compound exhibits characteristic signals in low (185.84 ppm, m, $^4J_{PCCCC}$ 1.5 Hz, $^3J_{HCCC}$ 9.6 Hz, $^4J_{HCCCC}$ 1.0 Hz) and high fields (51.92 ppm, dd, $^1J_{HC}$ 152.2 Hz, $^2J_{HCC}$ 2.8 Hz). The low-field signal belongs to the C-8a atom of the C=O group, while the high-field signal is due to the C-6 atom of the $Cl{-}C_6H(C{=}C)_2$ fragment of the quinoid type structure **VIb**. The C-3 carbon atom of **VIb** resonates in a lower field (120.18 ppm, dd, ${}^1J_{PC}$ 153.5 Hz, ${}^1J_{HC}$ 164.9 Hz) than that in heterocycle **IVb** (114.87 ppm, dd, ${}^1J_{PC}$ 166.3 Hr, ${}^1J_{HC}$ 172.0 Hz). The acyclic nature of this compound and *Z* configuration of the substituents at the C_3=C_4 bond is confirmed by the multiplicity and the magnitudes of the ${}^3J_{PCCC}$ and ${}^3J_{HCCC}$ constants of the C-5 and C-9 signals for *cis*- and *trans*-orientation of the phosphorus substituent: C-5, 139.15 ppm, ddd, ${}^3J_{PCCC}$(*cis*) 7.4 Hz, ${}^3J_{HCCC}$(*cis*) 4.8 Hz, ${}^3J_{HCCC}$(*trans*) 7.4 Hz; C-9, 135.87 ppm, dqd, ${}^3J_{PCCC}$(*trans*) 28.2 Hz, ${}^3J_{HCCC}$(*cis*) 7.1 Hz, ${}^3J_{HCCC}$(*trans*) 7.3 Hz. The *Z* configuration of substituents at the exocyclic multiple bond is also confirmed by the ease of cyclization of vinylphosphonate **VIb** into the benzophosphorine system (**IVc**).

I + **IIIb** + PCl_3



(**VIb**)

Scheme 3.

The fact of formation of compound **VIb** appears rather unusual; in all probability, this is related to the stabilizing steric effect of *tert*-butyl substituents.

Thus, despite the presence of bulky *tert*-butyl groups in *ortho*-benzoquinone (**I**), unusual reactions with phosphorus trichloride and arylacetylenes take place under rather mild conditions and result in the conversion of the *ortho*-benzoquinone structure into an oxybenzene structure fused to a phosphorine heterocycle; cyclization proceeds via intermediate quinoid structures. Regioselective chlorination of the bis(*tert*-butyl)phenyl substituent in the *para*-position relative to the endocyclic oxygen atom of the phosphorine ring also takes place during the reaction.

The NMR spectra were recorded on Bruker MSL-400 (162.0 MHz for ${}^{31}P$, 100.6 MHz for ${}^{13}C$) and Bruker WM-250 (${}^1H$, 250 MHz) spectrometers in $CDCl_3$ with respect to internal HMDS or external H_3PO_4.

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