

Reaction in a Three-component System Tetrachloro-*o*-benzoquinone–Arylacetylene–Phosphorus Trichloride*

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Abstract—Reaction in a three-component system tetrachloro-*o*-benzoquinone–arylacetylene–phosphorus trichloride was investigated with the use of NMR and IR spectroscopy and high resolution mass spectrometry. It was established that prevailingly formed 4-aryl-2-oxo-2,5,6,7,8-pentachlorobenzo[*e*]-1,2-oxaphosphorin-3-enes which on hydrolysis furnished 2-aryl-2-(1-hydroxy-2,3,4,5-tetrachlorophenyl)vinylphosphonic acids.

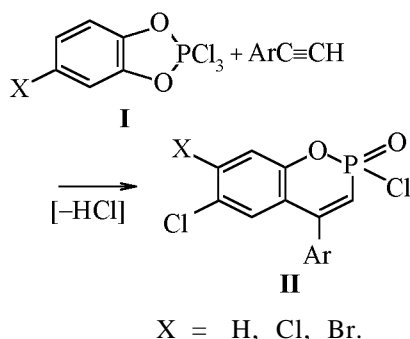
Reactions of substituted *o*-benzoquinones with P(III) derivatives are known to provide in a quantitative yield relatively stable compounds of pentacoordinate phosphorus, benzo[*d*]-λ⁵-1,3,2-dioxaphospholes [1, 2], that can be further used in the organic synthesis [3]. For instance, the products of reaction with phosphorus trichloride, substituted in the aromatic ring 2,2,2-trichlorobenzo[*d*]-λ⁵-1,3,2-dioxaphospholes, are fairly effective agents for replacement of a carbonyl group by a gem-dichloroalkyl moiety [4].

We recently demonstrated that substituted in the aromatic ring 2,2,2-trichlorobenzo[*d*]-λ⁵-1,3,2-dioxaphospholes (I) were capable to enter into an unusual reaction with arylacetylenes that resulted in formation of a heterocyclic system benzo[*e*]-λ⁴-1,2-

oxaphosphorin-3-ene (II) [5–7]. In the course of the reaction not only fairly readily formed a phosphorus–carbon bond and a phosphoryl group, but also occurred an uncommon *ipso*-substitution of an oxygen by a carbon atom and regioselective chlorination of the benzo-substituent in the para-position with respect to the endocyclic oxygen of the phosphorine heterocycle (II).

In some cases the preparation of initial phosphorane I is unfavorable because of its instability that puts a limit on this procedure. To avoid the necessity of phosphorane I synthesis from the corresponding pyrocatechol it seemed promising to use in reaction with arylacetylenes instead of compound I a combination of *o*-benzoquinone with phosphorus trichloride. Among available *o*-quinones the most interesting one is the sufficiently stable tetrachloro-*o*-benzoquinone. In reactions with phosphites this compound under very mild conditions provides P(V) derivatives, the corresponding monocyclic phosphoranes [8, 9]. The reaction with phosphorus trichloride occurs at heating and also yields a phosphorane, 2,2,2,4,5,6,7-heptachlorobenzo[*d*]-λ⁵-1,3,2-dioxaphosphole (III) [10].

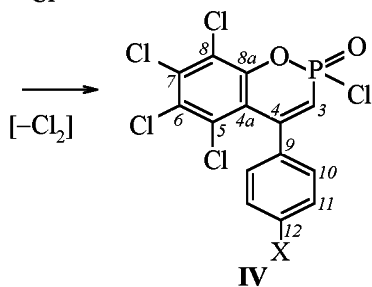
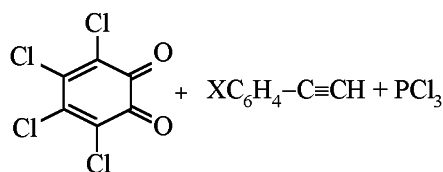
In this study we were first to show that a similar synthetic result, i.e., formation of benzo[*e*]-λ⁴-1,2-oxaphosphorin-3-ene derivative, was actually possible at the use of the three-component system tetrachloro-*o*-benzoquinone–arylacetylene–phosphorus trichloride (preliminary communications see [11, 12]. The addition of phosphorus trichloride to a mixture of *o*-chloranil with arylacetylene in dichloromethane at



† Deceased.

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10–15°C furnished prevalingly products that in the $^{31}\text{P}\{-^1\text{H}\}$ NMR spectra gave singlet signals at δ_{p} 19–21 ppm. In the ^{31}P NMR spectra registered without decoupling from protons the signals appear as doublets with coupling constants $^2J_{\text{PCH}}$ 25–27 Hz. The doublets with a similar coupling constant $^2J_{\text{PCH}}$ are also observed in the downfield part (5.5–6.5 ppm) of ^1H NMR spectra of the reaction mixtures. The content of these compound in the reaction mixture in different experiments amounts to 60–80%. In reaction with phenylacetylene we succeeded to isolate the main product as crystals easily suffering hydrolysis in air. The chemical shift δ_{p} indicates that the compounds obtained have a P–C bond. Taking in consideration the ^1H and ^{31}P NMR spectra (see the table) we assigned to the main products a structure of 3-aryl-2,5,6,7,8-pentachlorobenzo[e]- λ^4 -1,2-oxaphosphorin-3-enes (**IV**).



X = H (**a**), Me (**b**), Cl (**c**).

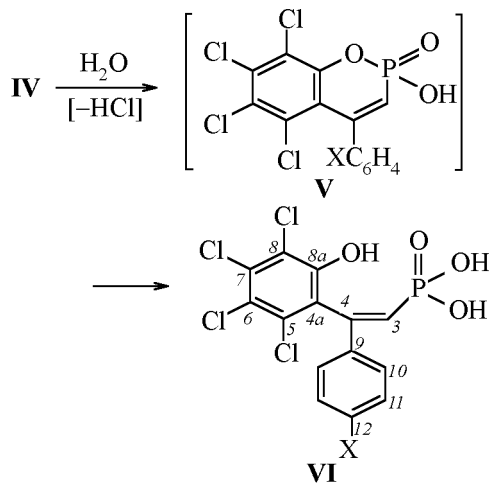
In the $^{13}\text{C}\{-^1\text{H}\}$ NMR spectra of the reaction mixtures taken after removing volatile impurities in the strong field a doublet belonging to C^3 carbon was observed. In the spectrum registered without proton decoupling the signal became a doublet of doublets with characteristic coupling constants $^1J_{\text{PC}}$ (158.2–158.8 Hz) and $^1J_{\text{HC}}$ (173.0–175.0 Hz). The assignment of the other signals in the spectra was carried out taking in consideration the published spectral data of similar in structure compounds [5–7].

The structure of benzophosphorines **IVa**, **c** was also confirmed by mass spectra obtained under the electron impact. In the mass spectra were observed peaks of m/z 412 and 446 corresponding to molecular ions $[M_{\text{IVa}}]^+$ and $[M_{\text{IVc}}]^+$. In the spectrum of compound **IVc** the peak of maximum intensity was that of ion $[M-\text{Cl}]^+$ with m/z 411 that

formed due to a loss of chlorine atom. The relative intensity of peaks caused by isotopes for all above ions corresponds to that calculated from their empirical formulas.

The chlorine evolved in the course of the reaction added to excess acetylene yielding the corresponding *cis*- and *trans*-isomers of dichlorostyrenes that were identified by spectral methods (spectral parameters of some among these compounds we had described before [7]).

Since we failed to isolate compounds **IVb**, **c** in the pure state the reaction mixtures after heating to 150–170°C in a vacuum of 0.1 mm Hg were subjected to hydrolysis in dioxane with the goal to separate individual reaction products. The compounds thus obtained were sufficiently easily crystallized from benzene or acetone, and according to $^{31}\text{P}\{-^1\text{H}\}$ NMR spectra these were also phosphonates. The structure of these phosphonates and also that obtained by hydrolysis of phosphorine **IVa** was determined from ^1H and ^{13}C NMR spectra (see the table). According to the spectral data the compounds formed are acyclic vinylphosphonic acids **VIa–c**. Thus the hydrolysis did not stop at the stage of phosphorines **V** formation.



X = H (**a**), Me (**b**), Cl (**c**).

In the ^{13}C NMR spectra of compounds **VI** the signal from C^3 carbon appears as a doublet of doublets with larger coupling constants $^1J_{\text{PC}}$ (170–190 Hz) than in the spectra of phosphorines **IV**. Acyclic structure of phosphonic acids **VI** is also evidenced by the value of the vicinal coupling constant $^3J_{\text{PCCC}^{4a}}$ (7.0–7.5 Hz) that is half as large as analogous constant in benzophosphorines **IV**. In the latter the coupling occurs by two channels, $\text{P}-\text{O}^l-\text{C}^{8a}-\text{C}^{4a}$ and $\text{P}-\text{C}^3-\text{C}^4-\text{C}^{4a}$.

Data of ^{13}C NMR spectra of compounds **IV** (40°C, CDCl_3) and **VI** ($\text{DMSO}-d_6$, 50°C), δ , ppm, J , Hz^a

Atom	Compound IV ^a	Compound IVb ^b	Compound IVc
C ³	120.63 d (d.d) (158.2, PC ³ ; 173.1, HC ³)	119.39 d (d.d) (158.8, PC ³ ; 175.0, HC ³)	120.96 d (d.d) (158.3, PC ³ ; 173.0, HC ³)
C ⁴	155.38 s (br.m) (4.1, HC ¹⁰ C ⁹ C ⁴ ; 3.9, HC ³ C ⁴)	155.35 s (d.t) (4.3, HC ¹⁰ C ⁹ C ⁴ ; 3.4, HC ³ C ⁴)	154.08 c (br.d.t) (4.3, HC ¹⁰ C ⁹ C ⁴ ; 3.6, HC ³ C ⁴)
C ^{4a}	121.91 d (d.d) (18.7, PC ³ C ⁴ C ^{4a} ; 8.8, HC ³ C ⁴ C ^{4a})	121.74 d (d.d) (18.7, PC ³ C ⁴ C ^{4a} ; 8.8, HC ³ C ⁴ C ^{4a})	121.53 d (d.d) (18.6, PC ³ C ⁴ C ^{4a} ; 8.7, HC ³ C ⁴ C ^{4a})
C ⁵	131.95 d (d) (2.6, PC ³ C ⁴ C ^{4a} C ⁵)	131.77 d (d) (2.6, PC ³ C ⁴ C ^{4a} C ⁵)	131.72 d (d) (2.6, PC ³ C ⁴ C ^{4a} C ⁵)
C ⁶	131.78 d (d) (1.9, POC ^{8a} C ^{4a} C ⁵ C ⁶)	131.50 d (d) (1.8, POC ^{8a} C ^{4a} C ⁵ C ⁶)	131.89 d (d) (1.9, POC ^{8a} C ^{4a} C ⁵ C ⁶)
C ⁷	136.25 d (d) (0.8–0.9, POC ^{8a} C ⁸ C ⁷)	135.88 s (s)	136.52 d (d) (0.9, POC ^{8a} C ⁸ C ⁷)
C ⁸	124.75 d (d) (7.4, POC ^{8a} C ⁸)	124.53 d (d) (7.5, POC ^{8a} C ⁸)	124.89 d (d) (7.5, POC ^{8a} C ⁸)
C ^{8a}	146.23 d (d) (9.5, POC ^{8a})	145.89 d (d) (9.4, POC ^{8a})	146.22 d (d) (9.7, POC ^{8a})
C ⁹	138.38 d (d.t.d) (19.4, PC ³ C ⁴ C ⁹ ; 7.1–7.2, HC ¹¹ C ¹⁰ C ⁹ ; 5.8–6.0, HC ³ C ⁴ C ⁹)	135.10 d (m) (19.6, PC ³ C ⁴ C ⁹ ; 7.8, HC ¹¹ C ¹⁰ C ⁹ ; 6.7, HC ³ C ⁴ C ⁹)	136.86 d (m) (19.9, PC ³ C ⁴ C ⁹ ; 7.8, HC ¹¹ C ¹⁰ C ⁹ ; 6.6, HC ³ C ⁴ C ⁹)
C ¹⁰	126.70 s (d.d.d) (161.4, HC ¹⁰ ; 6.7, HC ¹² C ¹¹ C ¹⁰ ; 6.2, HC ¹⁰ C ⁹ C ¹⁰)	128.53 s (d.d) (159.7, HC ¹⁰ ; 6.2, HC ¹⁰ C ⁹ C ¹⁰)	129.29 s (d.d) (162.2, HC ¹⁰ ; 6.5, HC ¹⁰ C ⁹ C ¹⁰)
C ¹¹	129.02 br.s (br.d.d) (163.1, HC ¹¹ ; 5.0–6.0, HC ¹¹ C ¹² C ¹¹)	129.37 br.s (br.d.m) (159.6, HC ¹¹)	128.06 br.s (d.d) (162.2, HC ¹¹ ; 6.5, HC ¹¹ C ¹² C ¹¹)
C ¹²	129.87 s (d.t) (161.8, HC ¹² ; 7.3, HC ¹⁰ C ¹¹ C ¹²)	139.59 s (m)	136.16 s (t.t) (10.5, HC ¹⁰ C ¹¹ C ¹² ; 3.5, HC ¹¹ C ¹²)
Atom	Compound VIa ($\text{DMF } d_7$) ^c	Compound VIb ^d	Compound VIc
C ³	119.93 d (d.d) (190.0, PC ³ ; 152.0, HC ³)	129.43 d (d.d) (170.2, PC ³ ; 148.5, HC ³)	123.78 d (d.d) (183.6, PC ³ ; 151.1, HC ³)
C ⁴	147.71 d (d.d.t) (3.7, PC ³ C ⁴ ; 3.7–4.0, HC ¹⁰ C ⁹ C ⁴ ; 3.7–4.0, HC ³ C ⁴)	144.69 d (d.d.t) (3.7, PC ³ C ⁴ ; 3.9, HC ¹⁰ C ⁹ C ⁴ ; 3.9, HC ³ C ⁴)	144.85 d (m) (4.4, PC ³ C ⁴)
C ^{4a}	126.86 d (d.d) (7.5, PC ³ C ⁴ C ^{4a} ; 10.5, HC ³ C ⁴ C ^{4a})	131.90 d (d.d) (7.0, PC ³ C ⁴ C ^{4a} ; 11.1, HC ³ C ⁴ C ^{4a})	127.91 d (d.d) (7.3, PC ³ C ⁴ C ^{4a} ; 10.5, HC ³ C ⁴ C ^{4a})
C ⁵	130.44 d (d) (2.0, PC ³ C ⁴ C ^{4a} C ⁵ ; 1.2, HC ³ C ⁴ C ^{4a} C ⁵)	131.0 d (d) (1.8, PC ³ C ⁴ C ^{4a} C ⁵)	131.15 d (br.s) (2.0, PC ³ C ⁴ C ^{4a} C ⁵)
C ⁶	122.09 s (s)	124.63 s (s)	121.87 s (s)
C ⁷	130.52 s (s)	130.0 s (s)	130.83 s (s)
C ⁸	119.89 s (s)	119.72 s (s)	120.64 s (s)
C ^{8a}	149.72 s (s)	155.39 s (br.s)	151.22 d (br.s) (1.5, PC ³ C ⁴ C ^{4a} C ^{8a})
C ⁹	137.15 d (d.t.d) (21.0, PC ³ C ⁴ C ⁹ ; 7.6, HC ¹¹ C ¹⁰ C ⁹ ; 5.0, HC ³ C ⁴ C ⁹)	138.01 d (d.t.d) (18.3, PC ³ C ⁴ C ⁹ ; 7.7, HC ¹¹ C ¹⁰ C ⁹ ; 6.8, HC ³ C ⁴ C ⁹)	136.59 d (d.t.d) (21.0, PC ³ C ⁴ C ⁹ ; 7.0, HC ¹¹ C ¹⁰ C ⁹ ; 6.5, HC ³ C ⁴ C ⁹)
C ¹⁰	125.38 s (br.d.d.d) (159.1, HC ¹⁰ ; 5.0–6.0, HC ¹⁰ C ⁹ C ¹⁰ ; 5.0–6.0, HC ¹² C ¹¹ C ¹⁰)	125.91 s (d.d) (158.0, HC ¹⁰ ; 6.5, HC ¹⁰ C ⁹ C ¹⁰)	128.80 s (d.d) (167.8, HC ¹⁰ ; 5.3, HC ¹⁰ C ⁹ C ¹⁰)
C ¹¹	127.31 s (br.d.d) (161.0, HC ¹¹ ; 7.8, HC ¹¹ C ¹² C ¹¹)	129.05 s (d.m) (158.0, HC ¹¹ ; 6.2, HC ¹¹ C ¹² C ¹¹ ; 6.1, HCC ¹² C ¹¹)	128.50 s (d.d) (162.3, HC ¹¹ ; 6.9, HC ¹¹ C ¹² C ¹¹)
C ¹²	127.97 s (d.t) (161.0, HC ¹² ; 7.2, HC ¹⁰ C ¹¹ C ¹²)	137.29 s (m) (6.8, HC ¹⁰ CC ¹² ; 6.5, HC ¹¹ C ¹²)	133.86 s (t.t) (10.6, HC ¹⁰ CC ¹² ; 2.9, HC ¹¹ C ¹²)

^a Multiplicity in ^{13}C NMR spectrum without decoupling from protons is given in parentheses.^b CH₃, 20.93 s (q.d) (126.8, HC; 4.3, HC¹¹C¹²C).^c 63.89 s (t.t.t) (dioxane; 143.0, HC; 3.7, HCC; 2.0, HCOC).^d CH₃, 20.71 s (q.t) (126.3, HC; 4.3, HC¹¹C¹²C).

Thus the reaction in the three-component system tetrachloro-*o*-benzoquinone-phosphorus trichloride-arylacetylene provides a possibility to prepare in one stage vinylphosphonic acids derivatives and extends the synthetic opportunities of the procedure described in [5–7].

EXPERIMENTAL

NMR spectra were measured on the following instruments: Bruker MSL-400 (^{13}C , ^{13}C -{1H}, 100.6 MHz; ^{31}P , ^{31}P -{1H}, 162.0 MHz), Bruker WM-250 (1H, 250 MHz), Bruker CXP-100 (36.48 MHz, ^{31}P , ^{31}P -{1H}) relative to HMDS as internal reference and H_3PO_4 as external reference. The ^1H and ^{13}C NMR spectra were registered at 30°C if not indicated otherwise. IR spectra were recorded on spectrophotometer Specord IR 75 from mulls in mineral oil placed between KBr plates. Mass spectrum of benzophosphorine **IVa** was measured on MKh-1310 instrument at ionizing electrons energy 70 eV, current of electrons collector 30 μA , sample input directly into the ion source at 120°C. The precise measurement of ion mass was performed automatically by reference peaks of perfluorokerosene. Relative error was no more than 5×10^{-5} amu. The mass spectrum of benzophosphorine **IVc** was obtained on Finnigan MAT-212 instrument under the same conditions. The processing of mass spectra was performed with the use of software MASPEC 2 system.

Reaction of tetrachloro-*o*-benzoquinone with phosphorus trichloride and phenylacetylene. To a solution of 6.2 g (0.025 mol) of tetrachloro-*o*-benzoquinone in 50 ml of benzene was added at stirring 2.6 ml (0.025 mol) of phenylacetylene and then dropwise 2.2 ml (0.026 mol) of phosphorus trichloride. Therewith the color of the reaction mixture turned from light-yellow to dark-brown and then gradually to light-brown. The reaction mixture was stirred at 10–15°C for 1 h, then the solvent was distilled off, and the residue was maintained in a vacuum of 0.1 mm Hg at heating to 160°C to remove excess acetylene and isomeric 1-phenyl-1,2-dichloroethenes. Then the glass-like substance obtained was dissolved in chloroform (20 ml) and kept at 0–5°C for 3–5 days. Therewith precipitated crystalline oxaphosphorine **IVa**, yield 27%, mp 179–180°C (from chloroform). Mass-spectrum, m/z (I_{rel} , %), ion composition: 420 (1.8), 419 (1.8), 418 (10.2), 417 (5.6), 416 (35.8), 414 (52.1), 413 (5.3), 412 (33.3) [$\text{C}_{14}\text{H}_6\text{Cl}_5\text{O}_2\text{P}$] $^+$; 384 (1.3), 383 (10.9), 381 (47.4), 380 (16.2), 379 (100), 378 (18.5), 377 (76.1) [$\text{C}_{14}\text{H}_6\text{Cl}_4\text{O}_2\text{P}$] $^+$.

^{31}P NMR spectrum (162.0 MHz, CDCl_3), δ , ppm: 15.2 d ($^2J_{\text{PCH}}$ 25.6 Hz). ^1H NMR spectrum (CDCl_3), δ , ppm, J , Hz: 7.54 m (5H, C_6H_5), 6.82 d (1H, PCH, $^2J_{\text{PCH}}$ 25.3). Found, %: C 40.47; H 1.57; Cl 43.08; P 7.27. $\text{C}_{14}\text{H}_6\text{Cl}_5\text{O}_2\text{P}$. Calculated, %: C 40.53; H 1.45; Cl 42.82; P 7.48.

The crystals and oily residue after chloroform removal were dissolved in 20 ml of dioxane and treated with excess water (2 ml). The solution formed was poured into 200 ml of water; the separated light-yellow oily substance was crystallized from chloroform containing a little amount of dioxane.

2-(1-Hydroxy-2,3,4,5-tetrachlorophenyl)-2-phenylvinylphosphonic acid (VIa) was obtained as a solvate with dioxane of 4:3 composition, yield 62%, mp 169–171°C (decomp.). IR spectrum, cm^{-1} : 466, 494, 575, 588, 620, 683, 695, 725, 760, 789, 823, 840, 870, 900, 941, 990, 1025–1028, 1080, 1130, 1160, 1190, 1220, 1260, 1270, 1280, 1290, 1310, 1320, 1560, 1612, 2250–2350 v.br, 2650–2750 v.br, 3100–3200 v.br. ^1H NMR spectrum (ethanol- d_6), δ , ppm, J , Hz: 7.34 br.s (5H, C_6H_5), 6.59 d (1H, PCH, $^2J_{\text{PCH}}$ 13.4), 3.67 s (6H, $\text{C}_4\text{H}_8\text{O}_2$). ^1H NMR spectrum (acetone- d_6), δ , ppm, J , Hz: 7.41 br.s (5H, C_6H_5), 6.74 d (1H, PCH, $^2J_{\text{PCH}}$ 13.3), 3.61 s (6H, $\text{C}_4\text{H}_8\text{O}_2$). ^{31}P NMR spectrum (162.0 MHz, ethanol- d_6), δ , ppm: 9.8 d ($^2J_{\text{PCH}}$ 13.5 Hz). Found, %: C 42.73; H 3.54; Cl 29.67; P 6.37. $4\text{C}_{14}\text{H}_9\text{Cl}_4\text{O}_4\text{P}-3\text{C}_4\text{H}_8\text{O}_2$. Calculated, %: C 42.50; H 3.13; Cl 29.58; P 6.46.

Reaction of tetrachloro-*o*-benzoquinone with phosphorus trichloride and *p*-methylphenylacetylene. To a solution of 5 g (0.02 mol) of tetrachloro-*o*-benzoquinone in 20 ml of benzene was added at stirring 2.35 g (0.02 mol) of *p*-methylphenylacetylene and then dropwise 1.9 ml (0.022 mol) of phosphorus trichloride. The reaction mixture was stirred at 10–15°C for 1–2 h, then the solvent was distilled off, and the residue was maintained in a vacuum of 0.1 mm Hg at heating to 160°C to remove excess acetylene and isomeric 1-(*p*-methylphenyl)-1,2-dichloroethenes. Then the glass-like light-brown substance containing 82% of 4-*p*-methylphenyl-2-oxo-2,5,6,7,8-pentachlorobenzo[*e*]-1,2-oxphosphorin-3-ene (**IVb**) was characterized by spectral methods. ^{31}P NMR spectrum (162.0 MHz, CDCl_3), δ , ppm: 16.3 d ($^2J_{\text{PCH}}$ 27.2 Hz). The oily compound was further dissolved in dioxane and treated with excess water. Dioxane and excess water were removed by distillation, the residue was dissolved in 20% solution of KOH, and then acidified with HCl to pH 5.0. Therewith partial-

ly formed a precipitate and separated an oily substance, both were separated and crystallized from benzene and acetone. 2-(1-Hydroxy-2,3,4,5-tetrachlorophenyl)-2-(*p*-methylphenyl)vinylphosphonic acid (**VIb**) was obtained in 47% yield, mp 176–178°C. ^{31}P NMR spectrum (36.48 MHz, DMSO- d_6), δ , ppm: 9.7 d ($^2J_{\text{PCH}}$ 12.0 Hz). ^1H NMR spectrum (DMSO- d_6 , 50°C), δ , ppm, J , Hz: 7.07 and 6.94 two m [4H, AA'BB'-spectrum, $^3J(\text{H}_\text{A}\text{H}_\text{B})$ 8.1], 6.48 d (1H, PCH, $^2J_{\text{PCH}}$ 11.8), 2.25 s (3H, CH₃). IR spectrum, cm⁻¹: 2250–2350 v.br, 2730–2780 v.br, 2360–2330 v.br, 1716, 1608, 1550, 1511, 1316, 1311, 1274, 1266 sh, 1158, 1092, 1108 sh, 1056, 985, 967, 922, 898, 830, 802, 754, 722, 677, 616, 564, 500, 484, 472. Found, %: C 41.92; H 2.81; Cl 33.23; P 7.49. C₁₅H₁₁Cl₄O₄P. Calculated, %: C 42.05; H 2.57; Cl 33.18; P 7.27.

Reaction of tetrachloro-*o*-benzoquinone with phosphorus trichloride and *p*-chlorophenylacetylene. To a solution of 4.8 g (0.019 mol) of tetrachloro-*o*-benzoquinone in 40 ml of benzene was added at stirring 2.7 g (0.02 mol) of 4-chlorophenylacetylene and then dropwise 2.0 ml (0.023 mol) of phosphorus trichloride. The reaction mixture was stirred at 10–15°C for 1–2 h, then the solvent was distilled off, and the residue was maintained in a vacuum of 0.1 mm Hg at heating to 160°C to remove excess acetylene and isomeric 1-(*p*-chlorophenyl)-1,2-dichloroethenes. Then the glass-like light-brown substance containing 77% of 2-oxo-4-*p*-chlorophenyl-2-oxo-2,5,6,7,8-pentachlorobenzo[*e*]-1,2-oxphosphorin-3-ene (**IVc**) was characterized by spectral methods. ^{31}P NMR spectrum (162.0 MHz, CDCl₃), δ , ppm: 15.2 d ($^2J_{\text{PCH}}$ 25.5 Hz). ^1H NMR spectrum (CDCl₃), δ , ppm: 6.57 d ($^2J_{\text{PCH}}$ 25.3 Hz). Mass spectrum, m/z (I_{rel} , %), ion composition: 446 (46.1) $[M]^+$, 447 (9.4), 448 (70.5), 449 (12.0), 450 (63.1), 451 (11.7), 452 (24.2), 453 (5.5), 454 (7.4), 411 (72.8) $[M-\text{Cl}]^+$, 412 (17.4), 413 (100.0), 414 (18.3), 415 (66.2), 416 (11.6), 417 (22.8). The oily substance was dissolved in dioxane and treated with excess water. The water-dioxane solution obtained was poured into 100 ml of 20% KOH solution and heated to 70°C. Insoluble resin was separated, and the water-dioxane mixture was acidified with HCl to pH 5 and then extracted with warm benzene (30–40°C). The benzene layer was separated, at cooling to 20°C formed a precipitate that was filtered off and washed with ether. 2-(1-Hydroxy-2,3,4,5-tetrachlorophenyl)-2-(*p*-chlorophenyl)vinylphosphonic acid (**VIc**) obtained was recrystallized from benzene and acetone,

yield 42%, mp 136–128°C. ^{31}P NMR spectrum (36.48 MHz, DMSO- d_6), δ , ppm: 9.4 d ($^2J_{\text{PCH}}$ 11.7 Hz). ^1H NMR spectrum (DMSO- d_6 , 50°C), δ , ppm, J , Hz: 7.41 and 7.34 two m [4H, AA'BB'-spectrum, $^3J(\text{H}_\text{A}\text{H}_\text{B})$ 8.9], 6.63 d (1H, PCH, $^2J_{\text{PCH}}$ 11.5). IR spectrum, cm⁻¹: 3290–3340 v.br, 2710–2730 v.br, 2280–2290 v.br, 2170–2180 sh, v.br, 1604, 1590, 1546, 1493, 1425, 1403, 1329, 1272, 1234, 1186, 1189 sh, 1159, 1094, 1077, 1013, 985, 974, 949, 860, 815 sh, 817 sh, 811, 780, 757, 740, 722, 709, 689, 678, 618, 567, 532, 500, 461, 428. Found, %: C 37.42; H 1.93; Cl 40.02; P 6.79. C₁₄H₈Cl₅O₄P. Calculated, %: C 37.46; H 1.78; Cl 39.78; P 6.91.

REFERENCES

- Ramirez, F., Desai, N.B., *J. Amer. Chem. Soc.*, 1960, vol. 82, no. 10, pp. 2652–2653; Ramirez, F., Desai, N.B., and Mitra, R.B., *J. Amer. Chem. Soc.*, 1961, vol. 83, no. 2, pp. 492; Kirillova, K.M. and Kukhtin, V.A., *Zh. Obshch. Khim.*, 1962, vol. 32, no. 7, pp. 2338–2340; Ramirez, F., *J. Amer. Chem. Soc.*, 1967, vol. 89, no. 10, pp. 2268–2272; Klimov, E.S., Bumber, A.A., and Okhlobystin, O.Yu., *Zh. Obshch. Khim.*, 1983, vol. 53, no. 8, pp. 1739–1742.
- Pudovik, A.N., Konovalova, I.V., and Ishmaeva, E.A., *Reaktsii i metody issledovaniya organicheskikh soedinenii* (Reactions and Methods of Investigation of Organic Compounds), Moscow: Khimiya, 1973, vol. 23.
- Cherkasov, R.A. and Pudovik, M.A., *Usp. Khim.*, 1994, vol. 63, no. 12, pp. 1087–1113.
- Gloede, J., *Z. Chem.*, 1982, vol. 22, no. 4, pp. 126–134.
- 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., and Il'yasov, A.V., *Zh. Obshch. Khim.*, 1998, vol. 68, no. 9, pp. 1482–1509.
- Mironov, V.F., Litvinov, I.A., Shtyrlina, A.A., Gubaidullin, A.T., Petrov, R.R., Konovalov, A.I., Azancheev, N.M., and Musin, R.Z., *Zh. Obshch. Khim.*, 2000, vol. 70, no. 7, pp. 1117–1132.
- Mironov, V.F., Petrov, R.R., Shtyrlina, A.A., Gubaidullin, A.T., Litvinov, I.A., Musin, R.Z., and Konovalov, A.I., *Zh. Obshch. Khim.*, 2001, vol. 71, no. 1, pp. 74–82.
- Ramirez, F., Bhatia, S.B., Patwardhan, A.V., Chen, E.H., and Smith, C.P., *J. Org. Chem.*, 1968, vol. 33, no. 1, pp. 20–24.
- Mironov, V.F., Burnaeva, L.A., Konovalova, I.V.,

- Khlopushina, G.A., Mavleev, R.A., and Chernov, P.P., *Zh. Obshch. Khim.*, 1993, vol. 63, no. 1, pp. 25–32.
10. Gloede, J. and Gross, H., *J. Prakt. Chem.*, 1970, vol. 312, pp. 326–334.
11. Mironov, V.F., Shtyrlina, A.A., Baronova, T.A., Varakshina, E.N., Alekseev, F.F., and Konovalov, A.I., Abstracts of Papers, *International Conference "Reaction Mechanisms and Organic Intermediates (140 Years of Organic Structural Theory)"*, St. Petersburg, Russia, 2001, pp. 162–163.
12. Mironov, V.F., Shtyrlina, A.A., Petrov, R.R., Baronova, T.A., Varaksina, E.N., and Konovalov, A.I., Abstracts of Papers, *XVth International Conference on Phosphorus Chemistry (ICPC15)*, Sendai, Japan, 2001.