Reaction of arylenedioxytrihalophosphoranes with acetylenes
11.* Electronic effect of the substituent in arylacetylene on the reaction rate

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The reactions of 2,2,2-trichlorobenzo-1,3,2-dioxaphosphole and its benzo-substituted derivatives with arylacetylenes containing strong +*M*-donors and −*M*-acceptors afford benzo[*e*]-1,2-oxaphosphinine 2-oxides (phosphacoumarins) in high yields. Studies by the competitive reaction method showed that the reaction rate is sensitive to the electronic nature of the substituent in arylacetylene. Thus, the introduction of +*M*-donors into the phenyl ring of arylacetylene leads to an increase in the reaction rate, whereas the introduction of −*M*-acceptors results in its substantial decrease. The molecular and supramolecular structures of selected 2-hydroxyphosphacoumarins and substituted vinylphosphonate, which is generated by the cleavage of the P-heterocycle, were studied by X-ray diffraction.

Key words: arylacetylene, 2,2,2-trichlorobenzo-1,3,2-dioxaphosphole, 2,2,2-trichloro-5-methylbenzo-1,3,2-dioxaphosphole, 4,7-bis(*tert*-butyl)-2,2,2-trichlorobenzo-1,3,2-dioxaphosphole, *ipso*-substitution of oxygen, benzo[*e*]-1,2-oxaphosphorinine 2-oxides, chlorination of the aromatic ring, reaction rate, electronic effect of the substituent, vinylphosphonate.

The development of facile and efficient methods for the synthesis of compounds containing the P—C bond is a topical problem in chemistry of heteroorganic compounds,[2—4] because they are widely used in various fields of chemistry, biology, and industry.[5] These compounds are often considered as phosphate analogs, which exhibit high and diverse biological activities and which are virtually not cleaved by hydrolases and transferases.[6,7] This is the reason why the synthesis of P—C analogs of different natural compounds (*e.g.*, aminophosphonates, P—C-sugars, P—C-nucleosides, and so on) has attracted firm interest.[8,9] Earlier,[10—14] we have developed a new approach to the synthesis of compounds containing the P—C bond, benzo[*e*]-1,2-oxaphosphinines (or phosphacoumarins), which are P—C analogs of coumarin. This approach is based on the reaction of 2,2,2-trichlorobenzo-1,3,2-dioxaphosphole (**1**) with arylacetylenes. The reaction involves the easy formation of the P—C bond, the *ipso*-substitution of oxygen by carbon, and the chlorination of the phenylene moiety at the *para* position with respect to the endocyclic oxygen atom of the heterocycle. In some cases, the above-mentioned transformations are accompanied by the *ipso*-substitution of the *tert*-butyl group by chlorine and the *ipso*-substitution of bromine by chlorine. More recently, many important features of the reaction, such as the effect of the nature of the halogen at the P^V atom, the effect of the nature of bulky substituents in the phenylene ring of 2,2,2-trihalobenzo-1,3,2-dioxaphosphole, the effect of the increase in the coordination number of the phosphorus atom from 5 to 6, and other factors have been elucidated (see the review[15]). However, no attention was given to such an important aspect of this multistep reaction as the influence of the electronic effect of substituents in the aromatic moiety of arylacetylene both on the synthetic result and the reaction rate as a whole. The aim of this work is to investigate the latter aspect.

Results and Discussion

The introduction of both nitro and methoxy groups into arylacetylene molecules does not cause a hindrance

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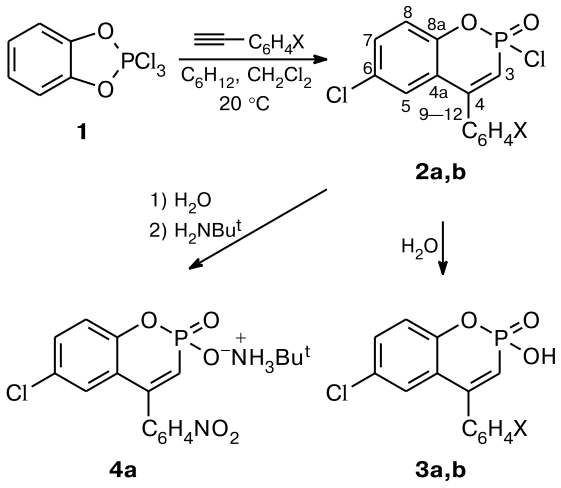
to the formation of phosphacoumarins, which substantially extends the synthetic potential of the reaction under consideration. Thus, the reaction of dioxaphosphole **1** with *p*-nitrophenylacetylene produces 2,6-dichloro-4-(4-nitrophenyl)benzo[*e*]-1,2-oxaphosphinine 2-oxide (**2a**) (Scheme 1). According to the ^{31}P NMR spectroscopic data (δ_P 18, $^2J_{HCP}$ = 25 Hz), the latter compound is the only phosphorus-containing reaction product. The mass spectrum of this product also contains only a molecular ion peak at *m/z* 355 corresponding to the molecular formula $C_{14}H_8Cl_2NO_4P$, which is indicative of the introduction of the chlorine atom into the molecule. The regiochemistry of the chlorination of the phenylene moiety was determined by ^{13}C and ^{13}C—{^1H} NMR spectroscopy. The absence of the coupling constant with the proton H(6) in the multiplet of the C(8) atom in the ^{13}C NMR spectrum confirms the presence of the chlorine atom at position 6 of oxaphosphinine **2a**.

Scheme 1

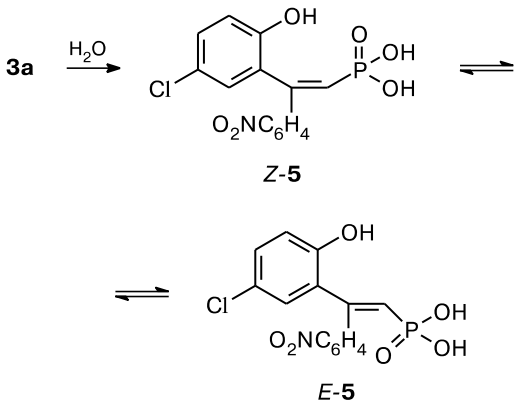


X = 4-NO_2 (**a**), 4-MeO (**b**)

After the hydrolysis and treatment with *tert*-butylamine, the corresponding phosphonic acid (**3a**) and its salt (**4a**) were isolated. Their structures were determined by NMR and IR spectroscopy. It should be noted that the storage of hydroxyphosphinine **3a** in wet DMSO over a long period of time results not only in the gradual cleavage of the P-heterocycle to form the *Z* isomer of phosphonic acid (*Z*-**5**) but also in the isomerization of the latter, apparently, to the thermodynamically more stable *E* isomer (*E*-**5**) (Scheme 2), This was established by ^1H and ^{31}P NMR spectroscopy. The reaction dynamics observed by ^{31}P NMR spectroscopy during a long period of time (DMSO, 20 °C) is illustrated by Fig. 1.

The reaction of benzodioxaphosphole **1** with *p*-methoxyphenylacetylene follows the same pathway. This reaction also gives the only phosphorus-containing product,

Scheme 2



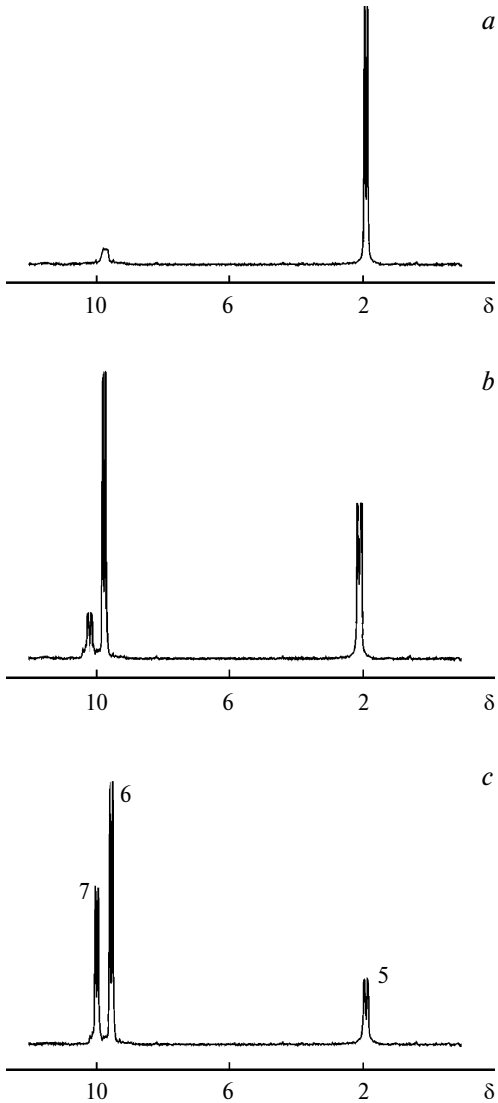


Fig. 1. Dynamics of the hydrolysis and isomerization of acid **3a** according to the ^{31}P NMR spectroscopic data in aqueous DMSO-d_6 (162.0 MHz) after 3 weeks (*a*), 11 months (*b*), and 26 months (*c*).

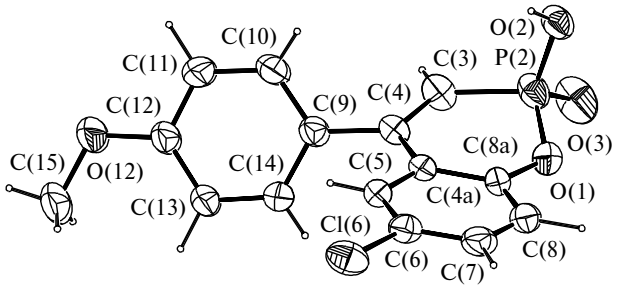


Fig. 2. Molecular structure of **3b** in the crystal and the atomic numbering scheme (here and in other figures, the thermal ellipsoids are drawn at the 30% probability level).

2,6-dichloro-4-(4-methoxyphenyl)benzo[*e*]-1,2-oxaphosphinine 2-oxide (**2b**). After the hydrolysis, phosphonic acid (**3b**) was isolated. In the $^{13}C—\{^1H\}$ NMR spectrum of this compound, the carbon atoms C(4a), C(8), and C(8a) appear as doublets with coupling constants of phosphorus, which corresponds to its cyclic nature. The heterocycle of molecule **3b** (Fig. 2, Tables 1—3) adopts a distorted (unsymmetrical) boat conformation (the O(1)C(8a)C(4a)C(4) fragment is planar within 0.002(4) Å; the C(3) and P(2) atoms deviate from this plane by 0.294(4) and 0.598(1) Å, respectively; the P(2)C(3)C(4)C(4a) fragment is planar within 0.016(4) Å; the O(1) and C(8a) atoms deviate from this plane by −0.516(3) and −0.236(4) Å, respectively). The oxygen atom O(2) substantially deviates from both planes (by 2.089(3) and −1.396(3) Å, respectively) and is in the axial position. The oxygen atom O(3) is in the equatorial position (the deviations are −0.046(3) and 0.897(3) Å, respectively). The dihedral angle between the O(1)C(8a)C(4a)C(4) and P(2)C(3)C(4)C(4a) planes is 12.7(2)°. The dihedral angle between the plane of the *para*-methoxyphenyl substituent at position 4 and the P(2)C(3)C(4)C(4a) plane (59.1(2)°) virtually does not allow this substituent to be conjugated with the C(3)=C(4) bond.

Table 1. Selected geometric parameters for structure **3b**

Parameter	Value
Bond length	*d*/Å
P(2)—O(1)	1.593(4)
P(2)—O(2)	1.519(3)
P(2)—O(3)	1.450(3)
P(2)—C(3)	1.744(4)
O(1)—C(8a)	1.375(5)
C(3)—C(4)	1.347(6)
C(4)—C(4a)	1.460(6)
C(4a)—C(5)	1.399(6)
C(4a)—C(8a)	1.398(6)
C(5)—C(6)	1.364(7)
C(6)—C(7)	1.366(6)
C(7)—C(8)	1.365(7)
C(8)—C(8a)	1.360(7)
Bond angle	ω/deg
O(1)—P(2)—O(2)	107.9(2)
O(1)—P(2)—O(3)	109.2(2)
O(2)—P(2)—C(3)	111.0(2)
O(3)—P(2)—C(3)	114.8(2)
P(2)—O(1)—C(8a)	123.4(3)
P(2)—C(3)—C(4)	121.2(3)
Torsion angle	θ/deg
O(2)—P(2)—O(1)—C(8a)	85.2(3)
O(3)—P(2)—O(1)—C(8a)	−155.1(3)
P(2)—C(3)—C(4)—C(4a)	3.5(5)
C(3)—C(4)—C(4a)—C(8a)	−14.5(6)
C(3)—C(4)—C(9)—C(10)	−56.8(6)

In the crystal, the molecules are linked to each other by O(2)—H(2)...O(3′) hydrogen bonds (see Table 2) to form chains along the crystallographic 0*a* axis (Fig. 3).

An analysis of the results of these reactions and a comparison of these reaction products with the reaction products of phosphorane **1** with phenylacetylene[11] show that the electron-donating methoxy group and the electron-withdrawing nitro group in the aromatic moiety of acetylene have no effect on the regiochemistry of the chlorination of the arylene moiety of oxaphosphinines, but affect the reaction rate, which is confirmed by the $^{31}P—\{^1H\}$ NMR dynamic experiment. Thus, the reaction with *p*-methoxyphenylacetylene occurs virtually immediately and is accompanied by a strong *exo* effect, whereas the reaction with *p*-nitrophenylacetylene is slower, as evidenced by the presence of the signal of the starting phosphorane (δ_P −26) along with the signal of the reaction product in the ^{31}P NMR spectrum recorded 5 min after the mixing of the reagents.

The reaction of 2,2,2-trichloro-5-methylbenzo-1,3,2-dioxaphosphole (**6**) with *p*-nitrophenylacetylene is characterized by lower selectivity of the *ipso*-substitution of the oxygen atom and the chlorination of the arene moiety

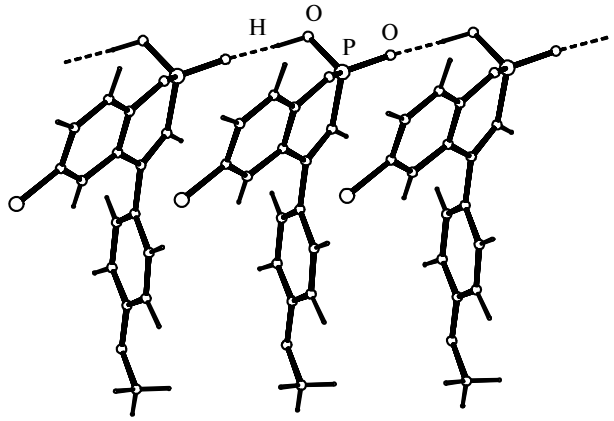


Fig. 3. Hydrogen bond network in the crystal of compound **3b**.

Table 2. Hydrogen bond parameters in the crystals of compounds **3b** and **24** (D is the donor, A is the acceptor)

D—H···A	*d*/Å			D—H—A angle /deg	Symmetry operation
	D—H	H···A	D···A		
			3b		
O(2)—H(2)···O(3′)	0.92(2)	1.49(2)	2.407(4)	176(6)	$1 + x, y, z$
			24		
O(3)—H(3)···O(50)	0.82(3)	1.74(4)	2.518(5)	160(3)	$1 - x, 1 - y, -z$
O(4)—H(4)···O(2′)	0.84(3)	1.71(3)	2.557(4)	176(4)	$2 - x, 1 - y, -z$
O(1)—H(1)···O(2)	0.84(3)	2.24(3)	2.978(4)	147(5)	—

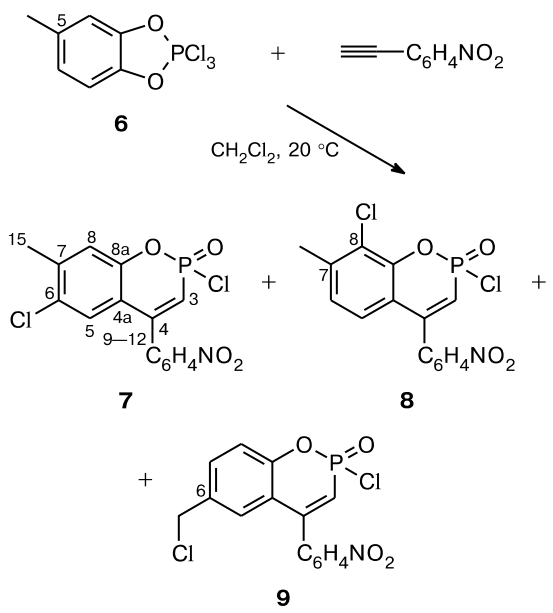
annulated to the P-heterocycle (compared to the corresponding reaction of phenylacetylene[16]). Three reaction products of oxaphosphinine nature, *viz.*, compounds **7**, **8**, and **9**, are formed in a ratio of 13.8 : 2.8 : 1 (Scheme 3). Benzoxaphosphinine **7** is the major product characterized by the molecular ion peak at *m/z* 369 in the electron impact mass spectrum. The structures of minor compounds **8** and **9** were established by ^{1}H and ^{13}C NMR spectroscopy. In the ^{13}C NMR spectrum, compound **9** is characterized by a triplet at δ_C 40 assigned to the chloromethylbenzyl group.

The hydrolysis and fractional crystallization afforded oxaphosphinine **10** (Scheme 4), whose storage in DMSO resulted in the gradual cleavage of the oxaphosphinine ring to form acid **11**. The latter is manifested in the ^{31}P NMR spectrum as a doublet with $J_{HC(2)P}$ = 12.6 Hz at

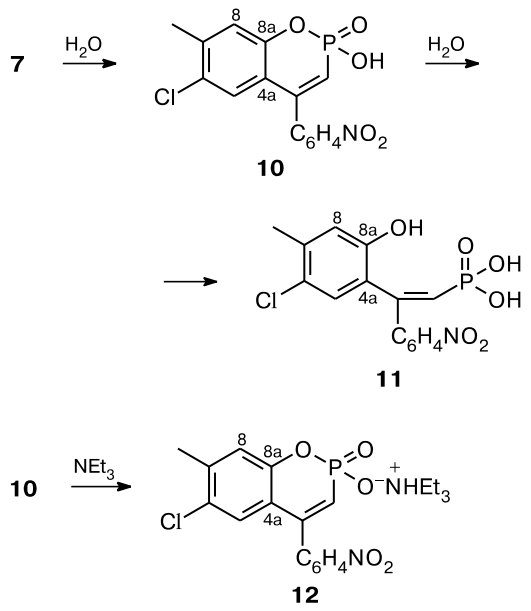
Table 3. Crystallographic parameters of compounds **3b**, **24**, and **26** and the X-ray data collection and structure refinement statistics

Parameter	**3b**	**24**	**26**
Crystal color, habit	Colorless, needle-like	Colorless, platelet-like	Colorless, prismatic
Molecular formula	$C_{15}H_{12}ClO_4P$	$C_{22}H_{27}ClO_6NP$, C_3H_6O	$C_{23}H_{27}Cl_2O_3P$
Molecular weight	645.33	525.94	453.32
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/n$	$P2_1/n$	P-1
Unit cell parameters			
a/Å	4.687(5)	9.040(2)	7.210(2)
b/Å	25.237(9)	9.889(3)	10.554(4)
c/Å	12.370(4)	29.157(7)	15.342(5)
α/deg	—	—	94.910(4)
β/deg	97.60(2)	90.673(3)	95.665(4)
γ/deg	—	—	96.244(4)
V/Å^3	1450(2)	2607(1)	1149.4(7)
Z	4	4	2
d_{calc}/g cm^{-3}	1.478	1.340	1.310
Absorption coefficient, μ(Mo)/cm^{-1}	3.86	2.52	3.73
F(000)	664	1112	476
Number of observed reflections	2847	5115	4412
R(int)	0.1443	0.0384	0.0322
Number of observed reflections with $I > 2\sigma(I)$	1115	3718	3089
R factors ($I > 2\sigma(I)$)	R = 0.0623, R_w = 0.0779	R = 0.0597, R_w = 0.1480	R = 0.0514, R_w = 0.1351
Goodness-of-fit	0.944	0.937	1.046
Number of parameters in refinement	195	336	269
hkl Ranges	$-5 \le h \le 5$, $-31 \le k \le 30$, $-15 \le l \le 15$	$-11 \le h \le 10$, $-12 \le k \le 12$, $-35 \le l \le 35$	$-8 \le h \le 8$, $-12 \le k \le 13$, $-18 \le l \le 18$

Scheme 3



Scheme 4



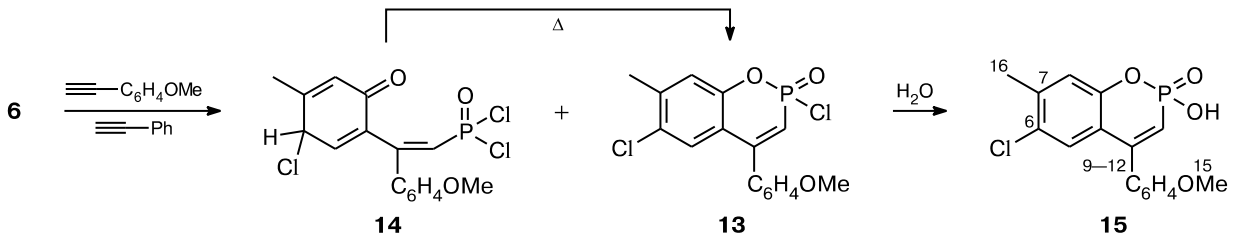
lower fields compared to cyclic oxaphosphinines. The constant $J_{PC(2)C(3)C(4)}$ = 7.3 Hz in the multiplet of the C(4) atom and the absence of the spin-spin coupling of the phosphorus nucleus with the carbon atoms C(8) and C(8a) in the ^{13}C NMR spectrum are also evidence for the acyclic nature of acid **11**. The treatment of phosphonic acid **10** with triethylamine gave ammonium salt **12**, in which the phosphonate anion retains the cyclic nature.

p-Methoxyphenylacetylene reacts with phosphole **6** more selectively than *p*-nitrophenylacetylene. After the storage over a long period of time (>10 days) or heating, oxaphosphinine **13** is formed as the only phosphorus-containing reaction product. The freshly prepared reaction product contains 12% of the intermediate 2-(5-chloro-4-methyl-6-oxocyclohexa-1,4-dienyl)-2-(4-methoxyphenyl) dichlorovinylphosphonate (**14**), which gives a doublet at δ_P 26.6 ($^2J_{PCH}$ = 31.0 Hz) in the ^{31}P NMR spectrum (earlier,[17] we have found related intermediates in the reaction of tetrachloro-*o*-benzoquinone with PCl_3 and arylacetylenes). The heating of vinylphosphonate **14** resulted in the elimination of HCl and the formation of oxaphosphinine **13** (Scheme 5). The structure of the latter compound was determined by NMR spectroscopy. After the hydrolysis, cyclic phosphonic acid (**15**) was isolated. The structure of the latter was also established by spectroscopic methods.

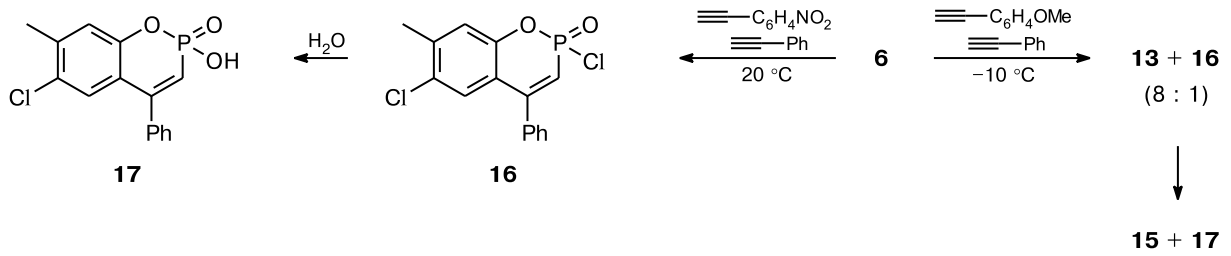
It should be noted that the P-heterocycle of acid **15** was not cleaved even after storage in aqueous DMSO over a long period of time due to the more efficient stabilization of the electron-donating methoxy group. Apparently, the electron-withdrawing nitro group substantially increases the electrophilicity of the phosphorus atom in phosphacoumarins, resulting in that it is more easily subjected to the attack by nucleophiles, even by such weak nucleophiles as water.

To qualitatively estimate the effect of the nature of substituents in the phenylacetylene moiety on the formation rate of phosphinines, we studied two model competitive reactions of dioxaphosphole **6** with an equimolar mixture of phenylacetylene and *p*-nitrophenylacetylene and with an equimolar mixture of phenylacetylene and *p*-methoxyphenylacetylene (Scheme 6). The reactions were carried out in dichloromethane in the presence of hexene at

Scheme 5



Scheme 6



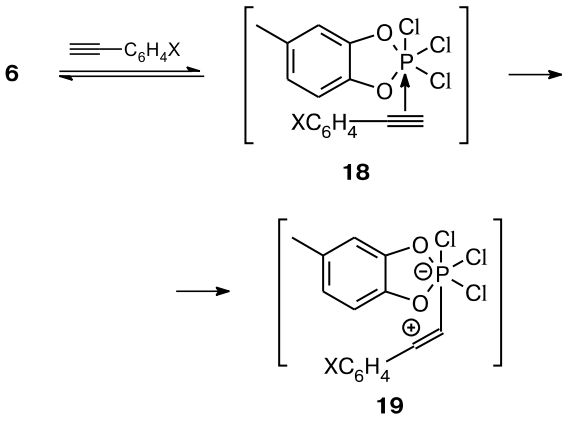
20 °C. The composition and the ratio of the components were controlled both based on acetylene and oxaphosphinines by ^{1}H and ^{31}P NMR spectroscopy and mass spectrometry. It appeared that the former reaction proceeds almost quantitatively with the involvement of phenylacetylene to form 2,6-dichloro-7-methyl-4-phenylbenzo[*e*]-1,2-oxaphosphinine 2-oxide (**16**) (this compound was characterized in the study[16]). In the latter case, the competitive reaction (*p*-methoxyphenylacetylene/phenylacetylene) gives two phosphorus-containing compounds, *viz.*, oxaphosphinines **13** and **16**, in a ratio of ~2 : 1. However, taking into account the high reactivity of acetylenes in the latter competitive reaction, it was performed also at lower temperature (−10 °C). In this case, the ratio of oxaphosphinines **13** and **16** was 8 : 1. After the hydrolysis of the reaction mixtures of both competitive reactions, 6-chloro-2-hydroxy-7-methyl-4-phenylbenzo[*e*]-1,2-oxaphosphinine 2-oxide (**17**) (the constants and spectroscopic parameters of this compound are identical to those reported in the study[16]) and compound **15** were isolated in high yields.

The competitive reactions show high selectivity to the nature of acetylene. The rate-determining step is very sensitive to the electronic nature of the group in the aryl substituent. The stronger the electron-donating character of this substituent, the higher the rate of the process as a whole.

According to the possible mechanism of the reaction of trihalobenzo-1,3,2-dioxaphospholes with terminal acetylenes, which has been considered in detail in the study,[15] it can be proposed that the nature of substituents in phenylacetylene affects the competition for the coordination with the phosphorus atom of benzo-1,3,2-dioxaphosphole (Lewis donor-acceptor interaction) in the formation of the π complex (**18**) (Scheme 7). Acetylenes containing stronger electron-donating groups form more stable π complexes and, consequently, these complexes will more readily undergo the reorganization to the σ complex (**19**) followed by the formation of the oxaphosphinine system.

The observed characteristic features of the reactions of *P*,*P*,*P*-trichlorobenzo-1,3,2-dioxaphospholes with arylacetylenes containing an electron-donating or -withdrawing substituent in the benzene ring were observed also in the reactions of these acetylenes with sterically hindered

Scheme 7



X = 4-OMe, 4-NO_2

4,7-di(*tert*-butyl)-2,2,2-trichlorobenzo-1,3,2-dioxaphosphole (**20**) (δ_P −29.8). On the whole, the reaction is slower due to the steric effect in the molecule of dioxaphosphole **20**. Thus, the reaction of the latter with *p*-nitrophenylacetylene (Scheme 8) initially gives the intermediate of the vinyl-quinoid type, *viz.*, 2-[3,6-di(*tert*-butyl)-3-chloro-6-oxocyclohexa-1,4-dienyl]-2-(4-nitrophenyl) dichlorovinylphosphonate (**21**), in one day. The content of this intermediate in the reaction mixture exceeds 80% (δ_P 25.2, $^{2}J_{PCH}$ = 31.5 Hz) in 3 days. The heating of this compound or its storage over a long period of time (>10 days) results in its transformation into the final reaction product, oxaphosphinine **22** (δ_P 14.6, $^{2}J_{PCH}$ = 25.2 Hz). The reaction dynamics was observed by ^{31}P NMR spectroscopy (CH_2Cl_2) and is illustrated by Fig. 4.

The introduction of the nitro group into the phenyl substituent located at position 4 of the benzoxaphosphinine ring leads to a decrease in the stability of cyclic derivative **23** to such an extent that the hydrolysis of compound **22** cannot be terminated in the step of the formation of **23**, and the reaction immediately gives acyclic phosphonic acid **24** (see Scheme 8). The treatment of the latter with triethylamine afforded salt **25**.

The molecular geometry of compound **24** isolated as the 1 : 1 acetone solvate was determined by X-ray dif-

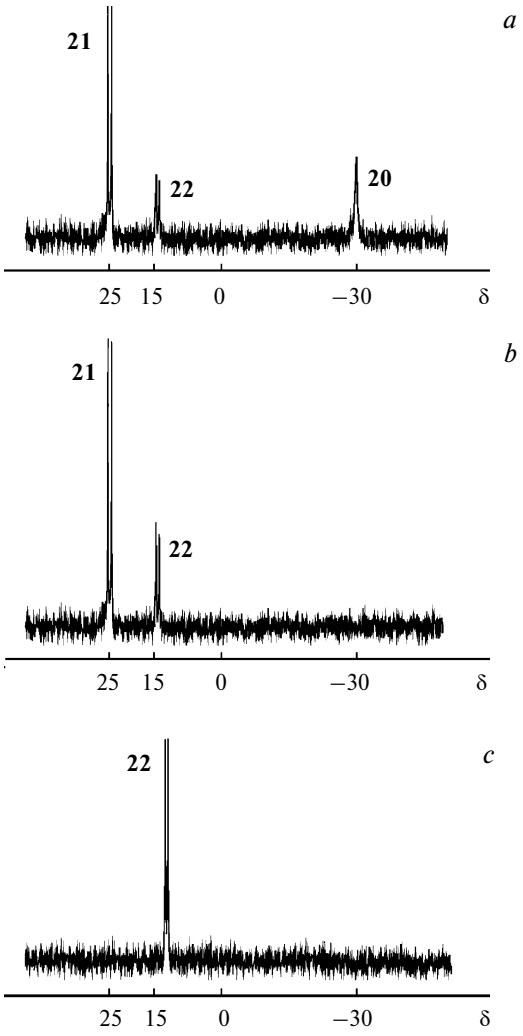


Fig. 4. Dynamics of changes in the composition of the reaction mixture of dioxaphosphole **20** and 4-nitrophenylacetylene with time according to the ^{31}P NMR spectroscopic data (36.48 MHz, CH_2Cl_2) after 1 (*a*), 3 (*b*), and 12 days (s).

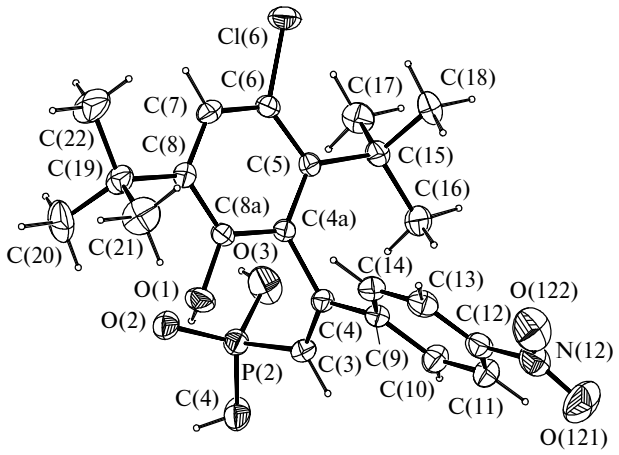


Fig. 5. Molecular structure of the acetone solvate of **24** and the atomic numbering scheme (the acetone molecule is not shown).

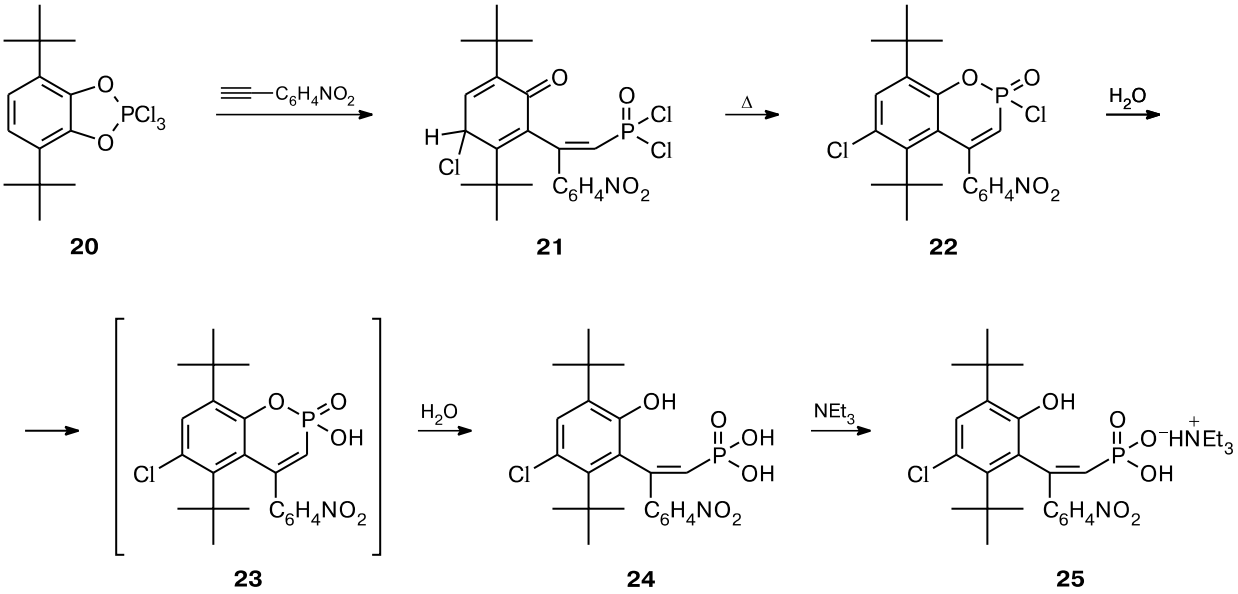
fraction (Fig. 5, Tables 2—4). The phenylene moiety C(4A)C(5)C(6)C(7)C(8)C(8a) is planar within 0.024(3) Å. The deviations of the atoms are as follows: Cl(6), 0.0635(9) Å; O(1), −0.033(3) Å; C(4), 0.193(3) Å; C(15), 0.061(3) Å; C(19), 0.051(4) Å. A substantial deviation of the C(4) atom from the phenylene moiety is apparently associated with the presence of two bulky substituents, such as the *para*-nitrophenyl and phosphorylmethyl groups, at this atom. The configuration of the substituents at the C(3)=C(4) double bond is retained (*Z*) despite the hydrolysis. Figure 6 shows the dimer of compound **24** formed *via* hydrogen bonds with the participation of the P(2)—O(4)—H(4) and O(2′)=P(2′) groups. Each molecule in the dimer is linked by the O(3)—H(3)···O(50) hydrogen bond to the acetone solvent molecule. The hydrogen bond parameters are given in Table 2.

p-Methoxyphenylacetylene reacts with phosphole **20** more vigorously without the formation of vinyl-quinoid-type intermediates at 0 °C to form oxaphosphinine **26** in

Table 4. Selected geometric parameters for structure **24**

Parameter	Value	Parameter	Value	Parameter	Value
Bond length	*d*/Å	Bond angle	ω/deg	Torsion angle	θ/deg
P(2)—O(2)	1.480(2)	O(2)—P(2)—O(3)	114.2(2)	O(2)—P(2)—C(3)—C(4)	−57.9(3)
P(2)—O(3)	1.542(3)	O(2)—P(2)—O(4)	113.1(2)	O(4)—P(2)—C(3)—C(4)	179.1(3)
P(2)—O(4)	1.546(3)	O(2)—P(2)—C(3)	112.7(1)	P(2)—C(3)—C(4)—C(9)	176.4(2)
P(2)—C(3)	1.775(3)	O(3)—P(2)—C(3)	103.8(2)	P(2)—C(3)—C(4)—C(4a)	4.3(4)
O(1)—C(8a)	1.378(4)	P(2)—C(3)—C(4)	125.8(2)	C(3)—C(4)—C(4a)—C(5)	−103.7(4)
C(3)—C(4)	1.335(4)	C(3)—C(4)—C(4a)	122.8(3)	C(3)—C(4)—C(9)—C(14)	−142.7(3)
C(4)—C(4a)	1.514(4)	C(4a)—C(4)—C(9)	116.3(2)	C(9)—C(4)—C(4a)—C(8a)	−90.3(3)
C(4)—C(9)	1.484(4)	C(4)—C(4a)—C(5)	125.4(3)	C(4)—C(4a)—C(5)—C(15)	5.7(5)
C(4a)—C(5)	1.422(4)	C(8a)—C(8)—C(19)	122.9(3)	C(4)—C(4a)—C(8a)—O(1)	−6.4(4)
C(4a)—C(8a)	1.403(4)	C(4a)—C(5)—C(15)	125.9(2)	C(15)—C(5)—C(6)—Cl(6)	2.6(4)
C(6)—C(7)	1.379(4)	Cl(6)—C(6)—C(5)	124.1(2)	C(19)—C(8)—C(8a)—O(1)	0.3(4)
C(7)—C(8)	1.373(4)				
C(8)—C(8a)	1.393(4)				

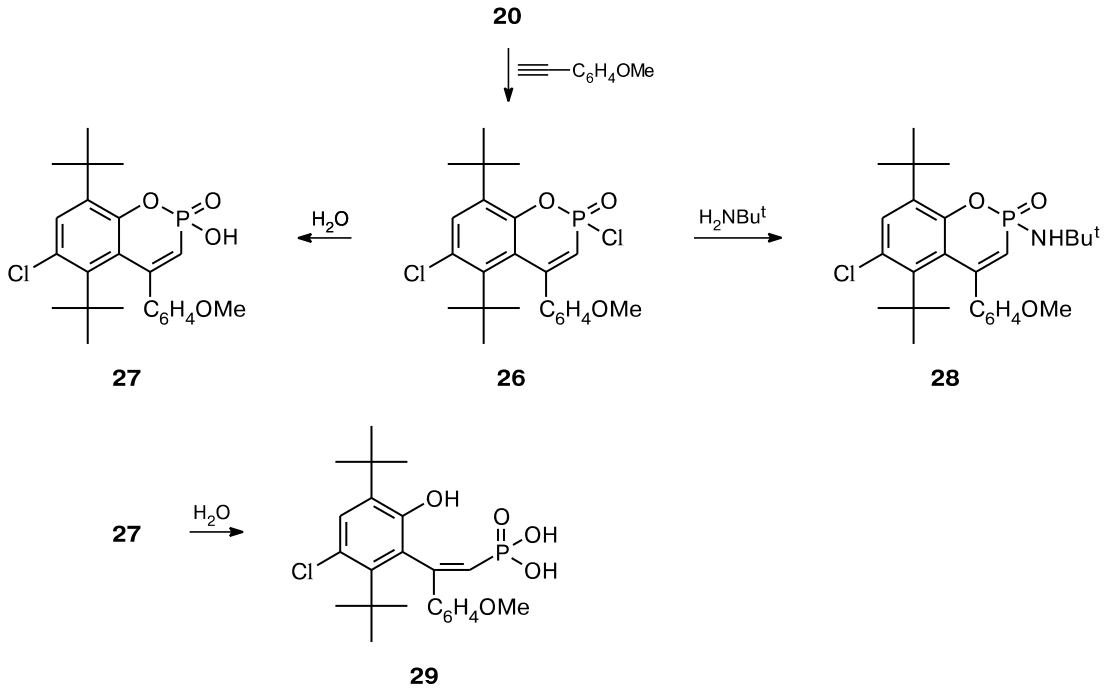
Scheme 8



high yield (Scheme 9). The characteristic feature of this compound is higher resistance of the phosphine heterocycle to the hydrolysis and aminolysis compared to compound **22**. This fact allowed us to synthesize cyclic amide **28** and spectroscopically detect phosphonic acid **27** (δ_P 2.1, $^2J_{PCH}$ = 15.6 Hz), which is rather rapidly hydrolyzed to form vinylphosphonic acid **29**.

The molecular structure of compound **26** in the crystal structure was determined by X-ray diffraction (Fig. 7, Tables 3 and 5). The heterocycle of **26** adopts a distorted (unsymmetrical) boat conformation and contains two planar groups, O(1)C(8a)C(4a)C(4) (planar within 0.091(2) Å) and P(2)C(3)C(4)C(4a) (planar within 0.033(2) Å). The other two atoms deviate from these planar groups by

Scheme 9



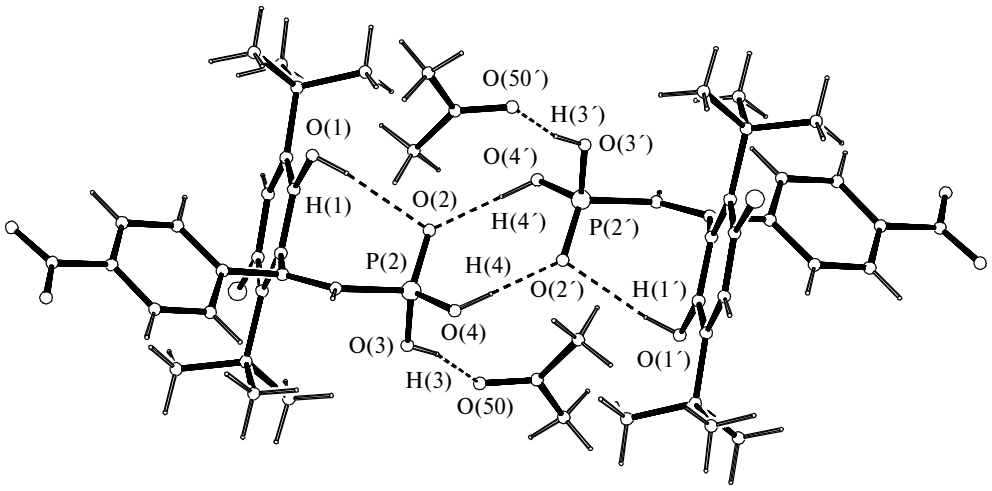


Fig. 6. Hydrogen bond network in the acetone solvate of **24** in the crystal.

−0.398(3) (C(3)) and −0.9487(8) Å (P(2)), 0.898(2) (O(1)) and 0.629(2) Å (C(8a)), respectively. The fact that the above-mentioned atoms deviate from the plane in the same direction and to a different extent is responsible for the unsymmetrical boat conformation. The chlorine atom Cl(2) substantially deviates from both planes (by −2.7808(9) and −1.7855(9) Å, respectively) and is in the axial position. The oxygen atom O(2) is in the equatorial position and is located closer to the above-mentioned planes (the deviations are −0.877(2) and 0.511(2) Å, respectively). A substantial deviation of the heterocycle from planarity is also evidenced by the dihedral angle between the planes O(1)C(8a)C(4a)C(4) and P(2)C(3)C(4)C(4a) (21.6(2)°). The dihedral angle between the plane of the *para*-methoxyphenyl substituent and the P(2)C(3)C(4)C(4a) plane is large (43.5(1)°) due to which, as in the case of molecule **3b**, the conjugation between this substituent and the C(3)=C(4) double bond is unlikely. The molecule of compound **26** contains the pentasubstituted sterically crowded benzene ring C(4a)C(5)C(6)C(7)C(8)C(8a), which is planar within 0.090(3) Å. The character of substitution leads to substantial deviations of the substituents from this plane. Thus, the Cl(6), O(1), C(4), C(15), and C(19) atoms deviate from this plane by 0.236(1), −0.086(2), 0.584(2), −0.611(3), and −0.150(3) Å, respectively. The largest deviations of the C(4) and C(15) atoms are associated with the steric repulsion between the *para*-methoxyphenyl and *tert*-butyl substituents. It is interesting that the C=C bond lengths in this benzene ring are also sensitive to the char-

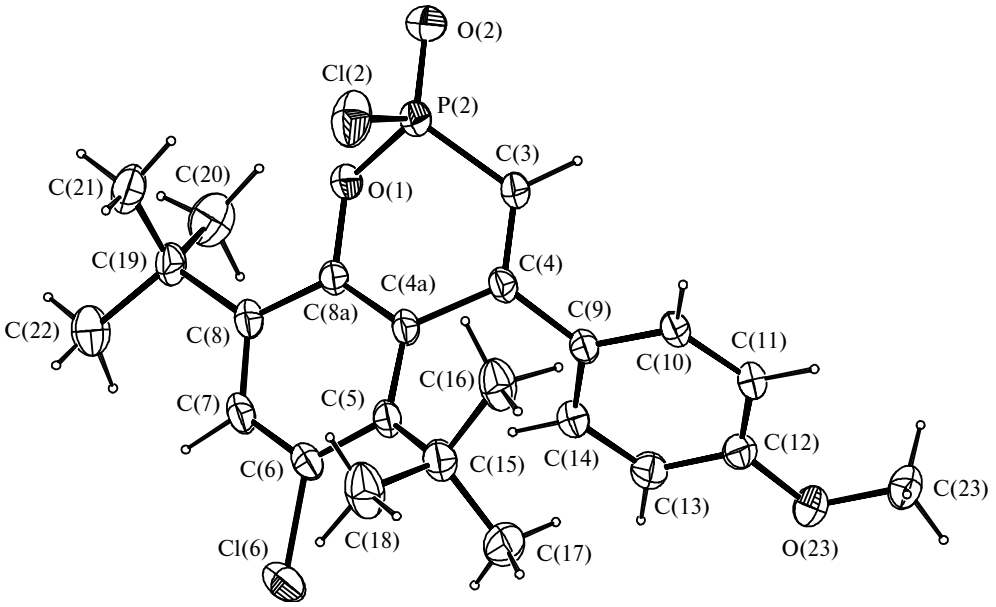


Fig. 7. Molecular structure of **26** in the crystal and the atomic numbering scheme.

Table 5. Selected geometric parameters for structure **26**

Parameter	Value
Bond length	*d*/Å
Cl(2)—P(2)	2.005(2)
Cl(6)—C(6)	1.745(3)
P(2)—O(1)	1.582(2)
P(2)—O(2)	1.449(2)
P(2)—C(3)	1.737(3)
O(1)—C(8a)	1.395(3)
C(3)—C(4)	1.346(4)
C(4)—C(4a)	1.496(3)
C(4a)—C(5)	1.417(3)
C(4a)—C(8a)	1.403(3)
C(5)—C(6)	1.389(4)
C(6)—C(7)	1.388(4)
C(7)—C(8)	1.372(4)
C(8)—C(8a)	1.398(3)
Bond angle	ω/deg
Cl(2)—P(2)—O(1)	102.52(8)
Cl(2)—P(2)—O(2)	112.0(1)
Cl(2)—P(2)—C(3)	108.8(1)
O(1)—P(2)—O(2)	112.8(1)
O(1)—P(2)—C(3)	101.1(1)
O(2)—P(2)—C(3)	118.1(1)
P(2)—C(3)—C(4)	118.3(2)
C(4)—C(4a)—C(5)	123.1(2)
C(4)—C(4a)—C(8a)	116.5(2)

Parameter	Value
Bond angle	ω/deg
C(4a)—C(5)—C(6)	113.8(2)
C(4a)—C(5)—C(15)	123.2(2)
Cl(6)—C(6)—C(7)	114.0(2)
C(8a)—C(8)—C(19)	123.4(2)
Torsion angle	θ/deg
Cl(2)—P(2)—O(1)—C(8a)	−64.6(2)
O(2)—P(2)—O(1)—C(8a)	174.8(2)
C(3)—P(2)—O(1)—C(8a)	47.7(2)
Cl(2)—P(2)—C(3)—C(4)	76.9(2)
O(1)—P(2)—C(3)—C(4)	−30.6(3)
O(2)—P(2)—C(3)—C(4)	−154.1(2)
P(2)—O(1)—C(8a)—C(4a)	−25.7(3)
P(2)—C(3)—C(4)—C(4a)	−6.9(3)
P(2)—C(3)—C(4)—C(9)	60.7(2)
C(3)—C(4)—C(4a)—C(8a)	36.3(3)
C(9)—C(4)—C(4a)—C(5)	40.0(3)
C(9)—C(4)—C(4a)—C(8a)	−131.3(2)
C(3)—C(4)—C(9)—C(10)	41.0(3)
C(4)—C(4a)—C(5)—C(15)	37.1(4)
C(8a)—C(4a)—C(5)—C(6)	17.8(3)
C(4)—C(4a)—C(8a)—O(1)	−19.9(3)
C(5)—C(4a)—C(8a)—C(8)	−12.6(4)
C(15)—C(5)—C(6)—Cl(6)	−25.6(4)
C(19)—C(8)—C(8a)—O(1)	−0.2(3)

acter of substitution in the ring. Thus, the tetrasubstituted C(8)=C(8a), C(8a)=C(4a), and C(4a)=C(5) bonds are much longer than the trisubstituted C(7)=C(8) and C(6)=C(7) bonds (see Table 5).

To summarize, the present study showed that the nature of the acetylene component plays a considerable role in the reaction with *P*,*P*,*P*-trihalobenzo-1,3,2-dioxaphospholes giving phosphacoumarin derivatives. The rate-determining step of this multistep reaction proved to be sensitive to the electronic nature of the substituent in the phenyl ring of arylacetylene. Thus, the presence of the +*M*-donor (OMe) substantially increases the reaction rate, whereas the introduction of the −*M*-acceptor (NO_2) substantially reduces the rate. The nature of the substituent also greatly affects the stability of intermediates in this reaction (vinyl-quinoid-type phosphonates) and the resistance of the resulting benzo[*e*]-1,2-oxaphosphinine derivatives to the hydrolysis.

Experimental

The NMR spectra were recorded on a Bruker Avance-400 instrument (400 MHz for ^{1}H, 100.6 MHz for ^{13}C, and 162 MHz for ^{31}P), unless otherwise mentioned, and on a Bruker CXP-100 instrument (36.48 MHz for ^{31}P). The IR spectra were measured on a Bruker Vector-22 spectrometer (Nujol mulls, KBr). Mass spectra were obtained on a DFS Thermo Electron Corporation instrument (Germany) at the ionizing electron energy of 70 eV using a direct inlet system. The temperature of the ion source was 280 °C. The vaporizer tube was heated in the temperature-programmed mode from 50 to 350 °C.

The X-ray diffraction data were collected from crystals of compounds **3b**, **24**, and **26** on a Bruker Smart APEX II CCD automated diffractometer (graphite monochromator, λ(Mo-Kα) = = 0.71073 Å, ω-scanning technique, 293 K). The semiempirical absorption correction was applied using the SADABS program.[18] The structures were solved by direct methods using the SIR program[19] and refined first isotropically and then anisotropically using the SHELXL-97 program package.[20] The hydroxy hydrogen atoms in the structures of **3b** and **24** were located in difference Fourier maps and refined isotropically. The other hydrogen atoms in the structures of **3b**, **24**, and **26** were positioned geometrically and refined using a riding model. All calculations were carried out with the use of the WinGX (see Ref. 21) and APEX2 (see Ref. 22) programs. All figures were prepared and intermolecular interactions were analyzed using the PLATON (see Ref. 23) and ORTEP (see Ref. 24) programs. The single-crystal X-ray diffraction studies of compounds **3b**, **24**, and **26** were performed at the Federal Spectral-Analytical Center for Collective Use on the basis of the Laboratory of Research by Diffraction Methods of the A. E. Arbuzov Institute of Organic and Physical Chemistry of the Kazan Scientific Center of the Russian Academy of Sciences. The crystallographic characteristics of the compounds and the X-ray data collection and structure refinement statistics are given in Table 3. The parameters of

intra- and intermolecular interactions (hydrogen bonds) are listed in Table 2.

Reaction of benzodioxaphosphole 1 with 4-nitrophenylacetylene. A solution of hex-1-ene (1.7 mL, 13.6 mmol) and 4-nitrophenylacetylene (1 g, 6.8 mmol) in CH_2Cl_2 (20 mL) was slowly added to a solution of phosphorane **1** (1.68 g, 6.8 mmol) in CH_2Cl_2 (5 mL) under a stream of argon. After the removal of the solvent and volatile products from the reaction mixture in a vacuum of 12 Torr (the external-heating temperature was 90—100 °C), the glassy pale-brown compound, **2,6-dichloro-4-(4-nitrophenyl)benzo[*e*]-1,2-oxaphosphinine 2-oxide (2a)**, was obtained and characterized by spectroscopic methods. MS, *m/z*: 355 $[M]^{+\cdot}$ ($C_{14}H_8Cl_2{}^{35}NO_4P$), 312 $[M - Cl]^+$. ^{1}H NMR ($CDCl_3$), δ: 6.46 (d, H(3), ^3J(PCH) = 22.2 Hz); 7.08 (d, H(5), ^4J(H(7)H(5)) = 2.5 Hz); 7.33 (d, H(8), ^3J(H(7)H(8)) = 8.3 Hz); 7.50 (d, H(7), ^4J(H(5)H(7)) = 2.5 Hz, ^3J(H(8)H(7)) = 8.3 Hz); 7.59 (m, H(10), AA´ part of AA´XX´ spectrum, ^3J(HCCH) = = 8.9 Hz); 8.40 (m, H(11), XX´ part of AA´XX´ spectrum, ^3J(HCCH) = 8.9 Hz). ^{13}C NMR ($CDCl_3$), δ_C: 117.13 (dd (d),* C(3), ^1J(PC(3)) = 154.4 Hz, ^1J(HC(3)) = 171.3 Hz); 153.32 (m (d), C(4), ^2J(PCC(4)) = 1.5 Hz); 122.04 (dddd (d), C(4a), ^3J(PCCC(4a)) = 18.0 Hz, ^3J(HC(3)CC(4a)) = 8.3 Hz, ^3J(HC(8)CC(4a)) = 7.0 Hz, ^2J(HC(5)C(4a)) = 1.2 Hz); 128.85 (dddd (d), C(5), ^4J(PCCCC(5)) = 1.6 Hz, ^1J(HC(5)) = 166.9 Hz, ^3J(HC(7)CC(5)) = 5.7 Hz, ^4J(HC(8)CCC(5)) = 1.5 Hz); 131.01 (dddd (d), C(6), ^4J(PCCCC(6)) = 1.5 Hz, ^3J(HC(8)CC(6)) = = 14.1 Hz, ^2J(HC(7)C(6)) = 4.6 Hz, ^2J(HC(5)C(6)) = 4.6 Hz); 132.99 (ddd (s), C(7), ^1J(HC(7)) = 170.5 Hz, ^3J(HC(5)CC(7)) = = 6.3 Hz, ^2J(HC(8)C(7)) = 1.0 Hz); 121.65 (dd (d), C(8), ^3J(POCC(8)) = 8.1 Hz, ^1J(HC(8)) = 169.0 Hz); 149.60 (dddd (d), C(8a), ^2J(POC(8a)) = 9.9 Hz, ^3J(HC(7)CC(8a)) = 10.2 Hz, ^3J(HC(5)CC(8a)) = 9.9 Hz, ^2J(HC(8)C(8a)) = 4.2 Hz); 142.83 (dtd (d), C(9), ^3J(PCCC(9)) = 20.9 Hz, ^3J(HC(11)CC(9)) = 7.7 Hz, ^3J(HC(3)CC(9)) = 6.2 Hz); 124.54 (dd (s), C(10), ^1J(HC(10)) = = 170.4 Hz, ^3J(HCCC(10)) = 4.8 Hz); 129.68 (dd (s), C(11), ^1J(HC(11)) = 166.9 Hz, ^3J(HCCC(11)) = 5.7 Hz); 147.74 (m (s), C(12)). ^{31}P NMR (CH_2Cl_2, 36.48 MHz), δ_P: 16.1 (d, ^2J(PCH) = = 22.2 Hz).

6-Chloro-2-hydroxy-4-(4-nitrophenyl)benzo[*e*]-1,2-oxaphosphinine 2-oxide (3a). A 20 : 1 mixture of water and acetone (16 mL) was added to phosphine **2a** (2.4 g, 6.7 mmol). The white precipitate that formed was filtered off and washed with a 3 : 1 dioxane—water mixture (4×2 mL) and then with diethyl ether (5×4 mL). Yield 2.12 g (93%), m.p. 321 °C (decomp.). 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. IR (Nujol mulls), 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 (DMSO-d_6), δ: 6.53 (d, H(3), ^2J(PC(3)H) = 16.4 Hz); 6.97 (d, H(5), ^4J(HC(7)CC(5)H) = 2.6 Hz); 7.34 (d, H(8), ^3J(HC(7)C(8)H) = 8.7 Hz); 7.52 (ddd, H(7), ^3J(HC(8)C(7)H) = = 8.7 Hz, ^4J(HC(5)CC(7)H) = 2.6 Hz, ^5J(POCCC(7)H) = 1.4 Hz); 7.68 (m, H(10), AA´ part of AA´XX´ spectrum); 8.33 (m, H(11), XX´ part of AA´XX´ spectrum). ^{13}C NMR (DMSO-d_6), δ_C: 119.70 (dd (d), C(3), ^1J(PC(3)) = 167.6 Hz, ^1J(HC(3)) = = 164.7 Hz); 148.80 (m (s), C(4)); 123.38 (dddm (d), C(4a), ^3J(PCCC(4a)) = 16.5 Hz, ^3J(HC(3)CC(4a)) = 8.1 Hz, ^3J(HC(8)CC(4a)) = 8.0 Hz); 127.68 (dd (s), C(5), ^1J(HC(5)) = = 165.8 Hz, ^3J(HC(7)CC(5)) = 5.1 Hz); 127.68 (ddd (s), C(6), ^3J(HC(8)CC(6)) = 11.4 Hz, ^2J(HC(7)C(6)) = 3.6 Hz, ^2J(HC(5)C(6)) = 3.6 Hz); 131.29 (dd (s), C(7), ^1J(HC(7)) = = 170.2 Hz, ^3J(HC(5)CC(7)) = 5.9 Hz); 121.82 (dd (d), C(8), ^1J(HC(8)) = 168.0 Hz, ^3J(POCC(8)) = 6.6 Hz); 150.49 (dddd (d), C(8a), ^2J(POC(8a)) = 7.3 Hz, ^3J(HC(5)CC(8a)) = 8.4 Hz, ^3J(HC(7)CC(8a)) = 8.4 Hz, ^2J(HC(8)C(8a)) = 3.7 Hz); 144.71 (dtd (d), C(9), ^3J(PCCC(9)) = 18.7 Hz, ^3J(HC(3)CC(9)) = = 7.3 Hz, ^3J(HC(11)CC(9)) = 7.3 Hz); 124.38 (dd (s), C(10), ^1J(HC(10)) = 170.6 Hz, ^2J(HC(11)C(10)) = 4.0 Hz); 130.36 (dd (s), C(11), ^1J(HC(11)) = 166.5 Hz, ^2J(HC(10)C(11)) = 6.6 Hz); 148.16 (m (s), C(12), ^3J(HC(10)CC(12)) = 9.2 Hz). ^{31}P NMR (DMSO-d_6, 36.48 MHz), δ_P: 3.3 (d, ^2J(PC(3)H) = 16.4 Hz).

***Z*-2-(5-Chloro-2-hydroxyphenyl)-2-(4-nitrophenyl)vinylphosphonic acid (*Z*-5)** (see the text). ^{1}H NMR (DMSO-d_6), δ: 6.19 (d, H(3), ^2J(PC(3)H) = 13.5 Hz); 6.86 (d, H(8), ^3J(HC(7)C(8)H) = 8.7 Hz); 7.21 (dd, H(7), ^3J(HC(8)C(7)H) = = 8.7 Hz, ^4J(HC(5)CC(7)H) = 2.7 Hz); 7.05 (d, H(5), ^4J(HC(7)CC(5)H) = 2.6 Hz); 7.54 (m, H(10), ^2J(HCCH) = = 8.9 Hz, AA´ part of AA´XX´ spectrum); 8.13 (m, H(11), ^2J(HCCH) = 8.9 Hz, XX´ part of AA´XX´ spectrum). ^{31}P NMR (DMSO-d_6), δ_P: 10.2 (d, ^2J(PC(3)H) = 13.5 Hz).

***E*-2-(5-Chloro-2-hydroxyphenyl)-2-(4-nitrophenyl)vinylphosphonic acid (*E*-5).** ^{1}H NMR (DMSO-d_6), δ: 6.44 (d, H(3), ^2J(PC(3)H) = 13.0 Hz); 6.81 (d, H(8), ^3J(HC(7)C(8)H) = = 8.5 Hz); 7.23 (dd, H(7), ^3J(HC(8)C(7)H) = 5.7 Hz, ^4J(HC(5)CC(7)H) = 2.9 Hz); 7.25 (dd, H(5), ^4J(HC(7)CC(5)H) = = 2.5 Hz, ^5J(PCCCC(5)H) = 2.5 Hz); 7.45 (m, H(10), ^2J(HCCH) = 8.9 Hz, AA´ part of AA´XX´ spectrum); 8.15 (m, H(11), ^2J(HCCH) = 8.9 Hz, XX´ part of AA´XX´ spectrum). ^{31}P NMR (DMSO-d_6), δ_P: 9.8 (d, ^2J(PC(3)H) = 13.0 Hz).

***tert*-Butylammonium 6-chloro-4-(4-nitrophenyl)benzo[*e*]-1,2-oxaphosphinine-2-oxide-2-oate (4a).** *tert*-Butylamine (0.19 mL, 1.72 mmol) was added to a solution of phosphine **3a** (0.29 g, 0.86 mmol) in diethyl ether (20 mL). The white precipitate that formed was filtered off and washed with diethyl ether (5×3 mL). Yield 0.33 g (93%), m.p. 237 °C. Found (%): C, 51.82; H, 5.13; Cl, 7.61; N, 6.72; P, 6.49. $C_{18}H_{20}ClN_2O_5P$. Calculated (%): C, 52.63; H, 4.91; Cl, 8.63; N, 6.82; P, 7.54. IR (KBr), ν/cm^{-1}: 434, 461, 480, 546, 565, 633, 655, 696, 728, 756, 805, 822, 836, 851, 870, 885, 948, 1016, 1072, 1090, 1113, 1151, 1197, 1223, 1264, 1348, 1376, 1401, 1470, 1519, 1549, 1585, 1638, 1886, 2004, 2169, 2341, 2360, 2539, 2627, 2736, 2913, 2983, 3033, 3451, 3558. ^{1}H NMR (DMSO-d_6—$CDCl_3$ (9 : 1)), δ: 1.23 (s, H(16)); 6.23 (d, H(3), ^2J(PC(3)H) = 15.1 Hz); 6.82 (d, H(5), ^4J(HC(7)CC(5)H) = 2.5 Hz); 7.05 (d, H(8), ^3J(HC(7)C(8)H) = = 8.7 Hz); 7.30 (ddd, H(7), ^3J(HC(8)C(7)H) = 8.7 Hz, ^4J(HC(5)CC(7)H) = 2.5 Hz, ^5J(POCCC(7)H) = 0.9 Hz); 7.57 (d, H(10), AA´ part of AA´XX´ spectrum, ^3J(HCCH) = 8.8 Hz); 7.87 (br.m, (NH_3^+)); 8.27 (d, H(11), XX´ part of AA´XX´ spectrum, ^3J(HCCH) = 8.8 Hz). ^{13}C NMR (DMSO-d_6—$CDCl_3$ (9 : 1)), δ_C: 127.29 (dd (d), C(3), ^1J(PC(3)) = 161.8 Hz, ^1J(HC(3)) = 157.0 Hz); 143.25 (br.m (s), C(4)); 124.82 (dddm (d), C(4a), ^3J(PCCC(4a)) = 15.0 Hz, ^3J(HC(3)CC(4a)) = 5.9 Hz, ^3J(HC(8)CC(4a)) = 5.9 Hz); 126.81 (dd (s), C(5), ^1J(HC(5)) = = 164.0 Hz, ^3J(HC(7)CC(5)) = 5.1 Hz); 125.53 (dm (s), C(6), ^3J(HC(8)CC(6)) = 7.4 Hz); 129.49 (dd (s), C(7), ^1J(HC(7)) = = 163.2 Hz, ^3J(HC(5)CC(7)) = 5.5 Hz); 121.61 (dd (d), C(8), ^1J(HC(8)) = 161.8 Hz, ^3J(POCC(8)) = 5.1 Hz); 152.70 (dddm (d),

* Hereinafter, the multiplicities of the signals in the ^{13}C—{^{1}H} NMR spectra are given in parentheses.

C(8a), ^2J(POC(8a)) = 7.3 Hz, ^3J(HC(5)CC(8a)) = 7.7 Hz, ^3J(HC(7)CC(8a)) = 7.7 Hz); 146.69 (dm (d), C(9), ^3J(PCCC(9)) = 7.3 Hz, ^3J(HC(11)CC(9)) = 7.6—7.7 Hz, ^3J(HC(13)CC(9)) = = 7.6—7.7 Hz, ^3J(HC(3)CC(9)) = 7.6—7.7 Hz); 130.11 (dd (s), C(10), ^1J(HC(10)) = 165.8 Hz, ^2J(HC(11)C(10)) = 6.6 Hz); 124.27 (dd (s), C(11), ^1J(HC(11)) = 169.5 Hz, ^2J(HC(10)C(11)) = 3.4 Hz); 147.62 (tm (s), C(12), ^3J(HC(10)CC(12)) = 8.8 Hz); 51.08 (m (s), C(15), ^2J(HCC(15)) = 3.7 Hz); 27.58 (br.q (s), C(16), ^1J(HC(16)) = 127.3 Hz). ^{31}P NMR (DMSO-d_6), δ_P: −3.5 (br.d, ^2J(PC(3)H) = 15.1 Hz).

Reaction of benzodioxaphosphole 1 with 4-methoxyphenylacetylene. Hex-1-ene (2.8 mL, 22.4 mmol) was added to a solution of phosphorane **1** (2.8 g, 11.4 mmol) in CH_2Cl_2 (7 mL), and then a solution of 4-methoxyphenylacetylene (1.5 g, 11.4 mmol) in CH_2Cl_2 (5 mL) was slowly added dropwise under a stream of argon. After the removal of the solvent and volatile products from the reaction mixture in a vacuum of 12 Torr (the external-heating temperature was 80—90 °C), the glassy pale-brown compound, **2,6-dichloro-4-(4-methoxyphenyl)benzo[*e*]-1,2-oxaphosphinine 2-oxide (2b)**, was obtained and characterized by spectroscopic methods. MS, *m/z*: 340 $[M]^{+\cdot}$ ($C_{15}H_{11}Cl_2{}^{35}O_3P$), 325 $[M - Me]^+$, 305 $[M - Cl]^+$. ^{1}H NMR ($CDCl_3$), δ: 3.90 (s, OMe); 6.34 (d, H(3), ^2J(PC(3)H) = 23.6 Hz); 7.04 (m, H(11), AA´ part of AA´XX´ spectrum); 7.28 (d, H(8), ^3J(HC(7)C(8)H) = = 8.5 Hz); 7.32 (d, H(5), ^4J(HC(7)CC(5)H) = 2.4 Hz); 7.33 (m, H(10), XX´ part of AA´XX´ spectrum); 7.45 (dd, H(7), ^3J(HC(8)C(7)H) = 8.5 Hz, ^4J(HC(5)CC(7)H) = 2.4 Hz, ^5J(POCCC(7)H) = 2.4 Hz). ^{13}C NMR ($CDCl_3$), δ_C: 114.31 (dd (d), C(3), ^1J(PC(3)) = 155.1 Hz, ^1J(HC(3)) = 170.9 Hz); 155.48 (m (d), C(4), ^2J(PCC(4a)) = 1.8 Hz); 123.04 (ddd (d), C(4a), ^3J(PCCC(4a)) = 17.2 Hz, ^3J(HC(3)CC(4a)) = 7.7 Hz, ^3J(HC(8)CC(4a)) = 7.7 Hz); 129.46 (dd (s), C(5), ^1J(HC(5)) = = 168.4 Hz, ^3J(HC(7)CC(5)) = 5.1 Hz); 129.46 (m (s), C(6), ^3J(HC(8)CC(6)) = 11.2 Hz); 132.06 (dd (s), C(7), ^1J(HC(7)) = = 170.2 Hz, ^3J(HC(5)CC(7)) = 6.2 Hz); 121.16 (dd (d), C(8), ^1J(HC(8)) = 168.7 Hz, ^3J(POCC(8)) = 8.1 Hz); 149.57 (dddd (d), C(8a), ^2J(POC(8a)) = 9.9 Hz, ^3J(HC(5)CC(8a)) = 9.9 Hz, ^3J(HC(5)CC(8a)) = 9.9 Hz, ^2J(HC(8)C(8a)) = 3.7 Hz); 137.77 (m (d), C(9), ^3J(PCCC(9)) = 11.4 Hz); 129.93 (dd (s), C(10), ^1J(HC(10)) = 159.9 Hz, ^2J(HC(11)C(10)) = 7.3 Hz); 114.52 (dd (s), C(11), ^1J(HC(11)) = 160.7 Hz, ^2J(HC(10)C(11)) = 4.8 Hz); 161.22 (m (s), C(12)); 55.49 (qm (s), OMe, ^1J(HC) = 144.5 Hz). ^{31}P NMR (CH_2Cl_2, 36.48 MHz), δ_P: 18.5 (d, ^2J(PCH) = 23.6 Hz).

6-Chloro-2-hydroxy-4-(4-methoxyphenyl)benzo[*e*]-1,2-oxaphosphinine 2-oxide (3b). A 20 : 1 mixture of acetone and water (16 mL) was added to phosphine **2b** (3.6 g, 10.9 mmol). The white precipitate that formed was filtered off and washed with dioxane (2×2 mL), a 3 : 1 dioxane—water mixture (3×2 mL), and diethyl ether (5×4 mL). Yield 2.48 g (71%), m.p. 272 °C. Found (%): C, 55.98; 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. IR (Nujol mulls), 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 (DMSO-d_6—$CDCl_3$ (1 : 4)), δ: 3.58 (s, H(13)); 6.07 (d, H(3), ^2J(PC(3)H) = 17.8 Hz); 6.93 (d, H(11), AA´ part of AA´XX´ spectrum); 7.09 (d, H(5), ^4J(HC(7)CC(5)H) = 2.2 Hz); 7.10 (d, H(8), ^3J(HC(7)C(8)H) = = 8.3 Hz); 7.22 (m, H(10), XX´ part of AA´XX´ spectrum); 7.26 (ddd, H(7), ^3J(HC(8)C(7)H) = 8.3 Hz, ^4J(HC(5)CC(7)H) = = 2.2 Hz, ^5J(POCCC(7)H) = 1.6 Hz). ^{13}C NMR (DMSO-d_6—$CDCl_3$ (1 : 4)), δ_C: 114.80 (dd (d), C(3), ^1J(PC(3)) = 171.7 Hz, ^1J(HC(3)) = 163.2 Hz); 151.18 (m (d), C(4), ^2J(PCC(4a)) = = 1.5 Hz); 123.38 (dddm (d), C(4a), ^3J(PCCC(4a)) = 16.1 Hz, ^3J(HC(3)CC(4a) = 5.5 Hz, ^3J(HC(8)CC(4a)) = 7.7 Hz); 127.86 (dd (s), C(5), ^1J(HC(5)) = 166.2 Hz, ^3J(HC(7)CC(5)) = 5.5 Hz); 127.47 (ddd (s), C(6), ^3J(HC(8)CC(6)) = 11.4 Hz, ^2J(HC(7)C(6)) = = 4.0 Hz, ^2J(HC(5)C(6)) = 4.0 Hz); 129.94 (dd (s), C(7), ^1J(HC(7)) = 169.1 Hz, ^3J(HC(5)CC(7)) = 5.9 Hz); 120.42 (dd (d), C(8), ^1J(HC(8)) = 166.2 Hz, ^3J(POCC(8)) = 7.4 Hz); 149.76 (dddd (d), C(8a), ^2J(POC(8a)) = 7.3 Hz, ^3J(HC(5)CC(8a)) = = 10.2 Hz, ^3J(HC(7)CC(8a)) = 10.2 Hz, ^2J(HC(8)C(8a)) = = 4.0 Hz); 129.91 (dt (d), C(9), ^3J(PCCC(9)) = 18.7 Hz, ^3J(HC(11)CC(9)) = 7.7 Hz); 129.26 (dd (s), C(10), ^1J(HC(10)) = = 159.2 Hz, ^2J(HC(11)C(10)) = 7.7 Hz); 113.74 (dd (s), C(11), ^1J(HC(11)) = 160.3 Hz, ^2J(HC(10)C(11)) = 4.4 Hz); 159.77 (m (s), C(12)); 54.91 (q (s), C(15), ^1J(HC(15)) = = 171.5 Hz). ^{31}P NMR (DMSO-d_6), δ_P: 4.7 (d, ^2J(PC(3)H) = = 17.8 Hz).

Reaction of benzodioxaphosphole 6 with 4-nitrophenylacetylene. 2,6-Dichloro-7-methyl-4-(4-nitrophenyl)benzo[*e*]-1,2-oxaphosphinine 2-oxide (7), 2,8-dichloro-7-methyl-4-(4-nitrophenyl)benzo[*e*]-1,2-oxaphosphinine 2-oxide (8), and 2-chloro-6-chloromethyl-4-(4-nitrophenyl)benzo[*e*]-1,2-oxaphosphinine 2-oxide (9). A solution of 4-nitrophenylacetylene (1.04 g, 7.07 mmol) in CH_2Cl_2 (16 mL) was added to a solution of phosphorane **6** (1.75 g, 6.64 mmol) and hex-1-ene (0.84 mL, 6.7 mmol) in CH_2Cl_2 (2 mL). The solvent and volatile products were removed from the reaction mixture in a vacuum of 12 Torr (the external-heating temperature was 70—90 °C), and the glassy pale-brown substance composed of compounds **7**—**9** was obtained. The latter were characterized by spectroscopic methods. MS of compounds **7**—**9**, *m/z* (I_{rel} (%)): 369 $[M]^{+\cdot}$ (10.1) ($C_{15}H_{10}Cl_2{}^{35}NO_4P$), 334 $[M - Cl]^+$ (17.3), 288 $[M - Cl - NO_2]^+$ (9.8), 270 $[M - P(O)OH - Cl]^+$ (3.1), 185 $[C_{13}H_{13}O]^+$ (100.0). ^{1}H NMR of compound **7** ($CDCl_3$), δ: 2.43 (s, H(15)); 6.38 (d, H(3), ^2J(PC(3)H) = 22.6 Hz); 7.06 (s, H(5)); 7.23 (s, H(8)); 7.58 (m, H(10), AA´ part of AA´XX´ spectrum); 8.34 (d, H(11), XX´ part of AA´XX´ spectrum). ^{13}C NMR of compound **7** ($CDCl_3$), δ_C: 20.39 (qd (s), CH_3, ^1J(HC) = 129.2 Hz, ^3J(HC(8)CC) = 4.3 Hz); 115.66 (dd (d), C(3), ^1J(PC(3)) = 154.8 Hz, ^1J(HC(3)) = 171.7 Hz); 153.40 (m (d), C(4), ^2J(PCC(4)) = = 2.3 Hz); 119.65 (m (d), C(4a), ^3J(PCCC(4a)) = 18.1 Hz); 128.88 (dd (d), C(5), ^1J(HC(5)) = 166.6 Hz, ^4J(PCCCC(5)) = = 1.4 Hz); 131.00 (m (d), C(6), ^5J(PCCCCC(6)) = 1.4 Hz); 142.19 (dq (s), C(7), ^2J(HCC(7)) = 6.2 Hz, ^3J(HC(5)CC(7)) = = 6.2 Hz); 122.08 (ddm (d), C(8), ^1J(HC(8)) = 165.5 Hz, ^3J(POCC(8)) = 8.1 Hz); 149.13 (ddd (d), C(8a), ^2J(POC(8a)) = = 10.1 Hz, ^3J(HC(5)CC(8a)) = 9.9 Hz, ^2J(HC(8)C(8a)) = 4.4 Hz); 142.87 (dt (d), C(9), ^3J(PCCC(9)) = 21.1 Hz, ^3J(HC(11)CC(9)) = = 7.9 Hz); 124.27 (dd (s), C(10), ^1J(HC(10)) = 170.2 Hz, ^2J(HC(11)C(10)) = 4.5 Hz); 129.58 (dd (s), C(11), ^1J(HC(11)) = = 165.9 Hz, ^2J(HC(10)C(11)) = 6.9 Hz); 148.71 (tt (s), C(12), ^3J(HC(10)CC(12)) = 9.4 Hz, ^2J(HC(11)C(12)) = 3.7 Hz). ^{31}P NMR (CH_2Cl_2, 36.48 MHz), δ_P: 15.9—16.1 (d, ^2J(PCH) = = 22.6—24.0 Hz) (compounds **7**—**9**).

6-Chloro-2-hydroxy-7-methyl-4-(4-nitrophenyl)benzo[*e*]-1,2-oxaphosphinine 2-oxide (10). A 20 : 1 mixture of acetone and water (16 mL) was added to a mixture of phosphines **7**—**9** (2.4 g). The white precipitate of compound **10** that formed was filtered off and washed with diethyl ether (5×4 mL). Yield 1.6 g (90%), m.p. 324 °C (decomp.). 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. IR (Nujol mulls), ν/cm^{-1}: 436, 462, 549, 566, 699, 730, 752, 809, 854, 869, 889, 1014, 1038, 1129, 1189, 1249, 1259, 1339, 1352, 1376, 1458, 1516, 1587, 1602, 2311, 3480. ^{1}H NMR (DMSO-d_6), δ: 2.35 (s, Me); 6.43 (d, H(3), ^2J(PC(3)H) = 16.6 Hz); 6.94 (s, H(5)); 7.33 (s, H(8)); 7.66 (m, H(10), AA´ part of AA´XX´ spectrum); 8.32 (m, H(11), XX´ part of AA´XX´ spectrum). ^{13}C NMR (DMSO-d_6), δ_C: 19.59 (qd (s), Me, ^1J(HC) = 128.7 Hz, ^3J(HC(8)CC) = = 4.2 Hz); 118.15 (dd (d), C(3), ^1J(PC(3)) = 168.0 Hz, ^1J(HC(3)) = = 164.6 Hz); 148.57 (m (br.s), C(4)); 120.82 (m (d), C(4a), ^3J(PCCC(4a)) = 16.5 Hz); 127.54 (d (s), C(5), ^1J(HC(5)) = = 164.3 Hz); 127.67 (dq (s), C(6), ^3J(HC(8)CC(6)) = 5.2 Hz, ^3J(HCCC(6)) = 4.7 Hz); 139.34 (dq (s), C(7), ^2J(HCC(7)) = = 6.2 Hz, ^3J(HC(5)CC(7)) = 6.2 Hz); 121.96 (ddq (d), C(8), ^1J(HC(8)) = 164.7 Hz, ^3J(POCC(8)) = 6.6 Hz, ^3J(HCCC(8)) = = 3.4 Hz); 149.87 (ddd (d), C(8a), ^2J(POC(8a)) = 7.0 Hz, ^3J(HC(5)CC(8a)) = 9.6 Hz, ^2J(HC(8)C(8a)) = 3.8 Hz); 144.45 (dtm (d), C(9), ^3J(PCCC(9)) = 18.7 Hz, ^3J(HC(11)CC(9)) = = 7.5 Hz); 124.05 (dd (s), C(10), ^1J(HC(10)) = 170.2 Hz, ^2J(HC(11)C(10)) = 4.4 Hz); 129.98 (dd (s), C(11), ^1J(HC(11)) = 166.8 Hz, ^2J(HC(10)C(11)) = 6.8 Hz); 147.83 (tt (s), C(12), ^3J(HC(10)CC(12)) = 9.5 Hz, ^2J(HC(11)C(12)) = 3.5 Hz). ^{31}P NMR (DMSO-d_6), δ_P: 4.5 (d, ^2J(PC(3)H) = 16.6 Hz).

***Z*-2-(5-Chloro-2-hydroxy-4-methyl)-2-(4-nitrophenyl)vinylphosphonic acid (11).** ^{1}H NMR (DMSO-d_6), δ: 2.26 (s, Me); 6.40 (d, H(3), ^2J(PC(3)H) = 12.6 Hz); 6.75 (s, H(8)); 7.25 (s, H(5)); 7.47 (m, H(10), AA´ part of AA´XX´ spectrum); 8.16 (m, H(11), XX´ part of AA´XX´ spectrum). ^{13}C NMR (DMSO-d_6), δ_C: 19.74 (qd (s), Me, ^1J(HC) = 128.0 Hz, ^3J(HC(8)CC) = = 4.4 Hz); 125.29 (dd (d), C(3), ^1J(PC(3)) = 181.9 Hz, ^1J(HC(3)) = = 150.3 Hz); 149.24 (m (d), C(4), ^2J(PCC(4)) = 4.8 Hz); 124.67 (m (d), C(4a), ^3J(PCCC(4a)) = 7.3 Hz); 131.24 (d (s), C(5), ^1J(HC(5)) = 165.3 Hz); 122.34 (m (s), C(6)); 136.41 (dq (s), C(7), ^2J(HCC(7)) = 6.0 Hz, ^3J(HC(5)CC(7)) = 6.0 Hz); 117.97 (dq (s), C(8), ^1J(HC(8)) = 158.8 Hz, ^3J(HCCC(8)) = 4.6 Hz); 153.50 (dm (s), C(8a), ^3J(HC(5)CC(8a)) = 8.80 Hz); 147.64 (m (d), C(9), ^3J(PCCC(9)) = 21.6 Hz); 123.63 (dd (s), C(10), ^1J(HC(10)) = 169.8 Hz, ^2J(HC(11)C(10)) = 4.1 Hz); 127.81 (dd (s), C(11), ^1J(HC(11)) = 164.6 Hz, ^3J(HC(10)C(11)) = = 6.8 Hz); 147.19 (tt (s), C(12), ^3J(HC(10)CC(12)) = 9.1 Hz, ^2J(HC(11)C(12)) = = 3.7 Hz). ^{31}P NMR (DMSO-d_6), δ_P: 10.2 (d, ^2J(PC(3)H) = 12.6 Hz).

Triethylammonium 6-chloro-7-methyl-4-(4-nitrophenyl)-benzo[*e*]-1,2-oxaphosphinine-2-oxide-2-oate (12). Triethylamine (0.084 mL, 0.57 mmol) was added to a solution of phosphine **10** (0.10 g, 0.28 mmol) in diethyl ether (5 mL). The white precipitate that formed was filtered off and washed with diethyl ether (5×1 mL). Yield 0.1 g (77%), m.p. 157 °C. Found (%): C, 55.27; H, 6.04; Cl, 7.18; N, 6.23; P, 6.45. $C_{21}H_{26}ClN_2O_5P$. Calculated (%): C, 55.70; H, 5.79; Cl, 7.83; N, 6.19; P, 6.84. IR (KBr), ν/cm^{-1}: 425, 438, 468, 482, 515, 538, 560, 617, 698, 728, 754, 822, 852, 873, 910, 918, 1014, 1068, 1107, 1129, 1171, 1216, 1247, 1348, 1375, 1389, 1452, 1485, 1521, 1580, 1595, 1803, 2477, 2608, 2918, 2948, 2985, 3037, 3106, 3430. ^{1}H NMR (DMSO-d_6—$CDCl_3$ (3 : 1)), δ: 1.17 (t, H(17), ^3J(HC(16)C(17)H) = = 7.3 Hz); 2.30 (s, H(15)); 3.03 (q, H(16), ^3J(HC(17)C(16)H) = = 7.3 Hz); 6.20 (d, H(3), ^2J(PC(3)H) = 15.5 Hz); 6.82 (s, H(5)); 7.06 (s, H(8)); 7.58 (m, H(10), AA´ part of AA´XX´ spectrum); 8.28 (m, H(11), XX´ part of AA´XX´ spectrum). ^{13}C NMR (DMSO-d_6—$CDCl_3$ (3 : 1)), δ_C: 126.36 (dd (d), C(3), ^1J(PC(3)) = = 162.1 Hz, ^1J(HC(3)) = 156.3 Hz); 143.16 (m (s), C(4)); 122.72 (m (d), C(4a), ^3J(PCCC(4a)) = 15.0 Hz, ^3J(HC(3)CC(4a)) = = 6.2—6.4 Hz, ^3J(HC(8)CC(4a)) = 6.2—6.4 Hz); 127.03 (d (s), C(5), ^1J(HC(5)) = 162.9 Hz); 125.85 (dq (s), C(6), ^3J(HC(8)CC(6)) = 7.4 Hz, ^3J(HC(15)CC(6)) = 5.5 Hz); 137.40 (dq (s), C(7), ^3J(HC(5)CC(7)) = 5.8—5.9 Hz, ^2J(HC(15)C(7)) = = 5.8—5.9 Hz); 122.25 (ddq (d), C(8), ^1J(HC(8)) = 161.8 Hz, ^3J(POCC(8)) = 5.5 Hz, ^3J(HC(15)CC(8)) = 5.4 Hz); 152.51 (ddd (d), C(8a), ^2J(POC(8a)) = 7.0 Hz, ^3J(HC(5)CC(8a)) = = 7.0 Hz, ^2J(HC(8)C(8a)) = 3.6 Hz); 146.80 (dt (d), C(9), ^3J(PCCC(9)) = 16.5 Hz, ^3J(HC(11)CC(9)) = 7.3 Hz); 124.29 (dd (s), C(10), ^1J(HC(10)) = 169.8 Hz, ^2J(HC(11)C(10)) = = 4.0 Hz); 130.11 (dd (s), C(11), ^1J(HC(11)) = 165.8 Hz, ^2J(HC(10)C(11)) = 7.0 Hz); 147.60 (m (s), C(12), ^3J(HC(10)CC(12)) = 9.5 Hz, ^2J(HC(11)C(12)) = 3.7 Hz); 19.85 (qd (s), C(15), ^1J(HC(15)) = 128.4 Hz, ^4J(HC(5)CCC(15)) = = 4.4 Hz); 46.00 (tm (s), C(16), ^1J(HC(16)) = 142.7 Hz); 8.94 (qm (s), C(17), ^1J(HC(17)) = 127.6 Hz). ^{31}P NMR (DMSO-d_6—$CDCl_3$ (3 : 1), 36.48 MHz), δ_P: 0.8 (br.d, ^2J(PC(3)H) = 15.6 Hz).

Reaction of benzodioxaphosphole 6 with 4-methoxyphenylacetylene. A solution of 4-methoxyphenylacetylene (1.51 g, 11.4 mmol) in CH_2Cl_2 (4 mL) was added to a solution of phosphorane **6** (2.7 g, 10.2 mmol) and hex-1-ene (1.3 mL, 10.4 mmol) in CH_2Cl_2 (2 mL). The solvent and volatile products were removed from the reaction mixture in a vacuum of 12 Torr (the external-heating temperature was 70—90 °C), and the glassy pale-brown compound, **2,6-dichloro-4-(4-methoxyphenyl)-7-methylbenzo[*e*]-1,2-oxaphosphinine 2-oxide (13)**, was obtained and characterized by spectroscopic methods. MS, *m*/*z* (I_{rel} (%)): 354 $[M]^{+\cdot}$ (32.5) ($C_{16}H_{13}Cl_2{}^{35}O_3P$), 339 $[M - Me]^+$ (1.6), 319 $[M - Cl]^+$ (7.2), 272 $[M - Cl - Me]^+$ (6.3), 234 (100.0), 185 $[C_{13}H_{13}O]^+$ (68.2). ^{1}H NMR of compound **13** ($CDCl_3$), δ: 2.36 (br.s, C(15)H(3)); 3.80 (s, OMe); 6.21 (d, H(3), ^2J(PC(3)H) = = 24.5 Hz); 6.95 (m, H(11), AA´ part of AA´XX´ spectrum, ^3J(HCCH) = 8.6 Hz); 7.14 (s, H(5)); 7.25 (s, H(8)); 7.25 (m, H(10), XX´ part of AA´XX´ spectrum, ^3J(HCCH) = 8.6 Hz). ^{13}C NMR ($CDCl_3$), δ_C: 19.91 (dq (s), Me, ^1J(HC) = 128.6 Hz, ^3J(HC(8)CC) = 4.6 Hz); 55.74 (q (s), MeO, ^1J(HC) = = 144.5 Hz); 115.76 (dd (d), (C(3), ^1J(PC(3)) = 169.4 Hz, ^1J(HC(3)) = 163.5 Hz); 153.80 (m (d), C(4), ^2J(PCC(4)) = = 1.5 Hz); 122.06 (m (d), C(4a), ^3J(PCCC(4a)) = 16.5 Hz); 128.30 (d (s), C(5), ^1J(HC(5)) = 164.6 Hz); 127.82 (dq (s), C(6), ^2J(HC(5)C(6)) = 5.6 Hz, ^3J(HCCC(6)) = 5.0) Hz; 139.22 (dq (s), C(7), ^3J(HC(5)CC(7)) = 6.3 Hz, ^2J(HCC(7)) = 6.3 Hz); 122.25 (ddq (d), C(8), ^1J(HC(8)) = 164.3 Hz, ^3J(POCC(8)) = = 7.0 Hz, ^3J(HCCC(8)) = 5.6 Hz); 150.31 (ddd (d), C(8a), ^2J(POC(8a)) = 7.0 Hz, ^3J(HC(5)CC(8a)) = 7.0 Hz, ^2J(HC(8)C(8a)) = 3.4 Hz); 130.53 (dt (d), C(9), ^3J(PCCC(9)) = = 18.7 Hz, ^3J(HC(11)CC(9)) = 7.8 Hz); 130.18 (dd (s), C(10), ^1J(HC(10)) = 159.5 Hz, ^2J(HC(11)C(10)) = 7.4 Hz); 114.70 (dd (s), C(11), ^1J(HC(11)) = 160.5 Hz, ^2J(HC(10)C(11)) = 4.7 Hz); 160.35 (m (s), C(12)). ^{31}P NMR (CH_2Cl_2, 36.48 MHz), δ_P: 16.0 (d, ^2J(PCH) = 24.5 Hz).

6-Chloro-2-hydroxy-4-(4-methoxyphenyl)-7-methylbenzo-[*e*]-1,2-oxaphosphinine 2-oxide (15). A 20 : 1 mixture of acetone and water (21 mL) was added to phosphine **13** (3.6 g, 10.1 mmol). The white precipitate that formed was filtered off and washed with diethyl ether (5×4 mL). Yield 2.87 g (84%), m.p. 286 °C. Found (%): C, 56.79; H, 4.87; Cl, 10.34; P, 9.05. $C_{16}H_{14}ClO_4P$. Calculated (%): C, 57.07; H, 4.19; Cl, 10.53; P, 9.20. IR (Nujol

mulls), ν/cm^{-1}: 415, 444, 463, 484, 521, 535, 553, 584, 631, 666, 722, 748, 782, 801, 820, 853, 870, 883, 890, 922, 1014, 1033, 1128, 1166, 1179, 1248, 1337, 1376, 1460, 1483, 1510, 1595, 1611, 2290, 2549, 2854, 2924, 2954, 3466. ^{1}H NMR (DMSO-d$_6$), δ: 2.36 (br.s, Me); 3.83 (s, OMe); 6.23 (d, H(3), ^2J(PC(3)H) = = 17.8 Hz); 7.07 (m, H(11), AA´ part of AA´XX´ spectrum); 7.08 (s, H(8)); 7.32 (br.s, H(5)); 7.33 (m, H(10), XX´ part of AA´XX´ spectrum). ^{13}C NMR (DMSO-d$_6$), δ$_C$: 115.76 (dd (d), C(3), ^1J(PC(3)) = 169.5 Hz, ^1J(HC(3)) = 163.5 Hz); 150.78 (m (d), C(4), ^2J(PCC(4)) = 1.5 Hz); 121.91 (m (d), C(4a), ^3J(PCCC(4a)) = 16.5 Hz); 128.30 (d (s), C(5), ^1J(HC(5)) = = 164.6 Hz); 127.82 (dq (s), C(6), ^2J(HC(5)C(6)) = 5.6 Hz, ^3J(H(3)CC(7)C(6)) = 5.0 Hz); 139.22 (dq (s), C(7), ^2J(HC(8)C(7)) = 6.3 Hz, ^2J(H(3)CC(7)) = 6.3 Hz); 122.23 (ddq (d), C(8), ^1J(HC(8)) = 163.4 Hz, ^3J(H(3)CC(7)C(8)) = 6.1 Hz, ^3J(POC(8a)C(8)) = 7.0 Hz); 150.29 (ddd (d), C(8a), ^2J(POC(8a)) = 7.0 Hz, ^3J(HC(5)CC(8a)) = 7.0 Hz, ^2J(HC(8)C(8a)) = = 3.8 Hz); 130.52 (dm (d), C(9), ^3J(PCCC(9)) = 18.7 Hz, ^2J(HCC(9) = 7.8 Hz); 130.18 (dd (s), C(10), ^1J(HC(10)) = = 159.5 Hz, ^2J(HC(11)C(10)) = 7.4 Hz); 114.70 (dd (s), C(11), ^1J(HC(11)) = 160.5 Hz, ^2J(HC(10)C(11)) = 4.7 Hz); 160.35 (m (s), C(12)); 19.91 (qd (s), Me, ^1J(HC) = 128.7 Hz, ^3J(HC(8)CCH) = 4.1 Hz); 55.74 (q (s), OMe, ^1J(HC) = 144.5 Hz). ^{31}P NMR (DMSO-d$_6$), δ$_P$: 5.4 (d, ^2J(PC(3)H) = 17.8 Hz).

Competitive reaction of 2,2,2-trichloro-5-methylbenzo[*d*]-1,3,2-dioxaphosphole 6 with a mixture of 4-nitrophenyl- and phenylacetylene. A solution of 4-nitrophenylacetylene (0.31 g, 2.1 mmol) and phenylacetylene (0.22 g, 2.1 mmol) in CH_2Cl_2 (6 mL) was rapidly added to a solution of phosphorane **6** (0.50 g, 1.9 mmol) and hex-1-ene (0.24 mL, 1.9 mmol) in CH_2Cl_2 (2 mL), The ^{31}P NMR spectrum of the reaction mixture (CH_2Cl_2, 36.48 MHz), δ$_P$: 18.9 (d, ^2J(PCH) = 23.1 Hz). This spectrum corresponds to compound **16**.

Competitive reaction of benzodioxaphosphole 6 with a mixture of 4-methoxyphenyl- and phenylacetylene. A solution of 4-nitrophenylacetylene (0.32 g, 2.4 mmol) and phenylacetylene (0.25 g, 2.4 mmol) in CH_2Cl_2 (5 mL) was rapidly added to a solution of phosphorane **6** (0.58 g, 2.2 mmol) and hex-1-ene (0.28 mL, 2.2 mmol) in CH_2Cl_2 (2 mL) at 20 °C. The ^{31}P NMR spectrum of the reaction mixture (CH_2Cl_2, 36.48 MHz), δ$_P$: 18.9 (d, ^2J(PCH) = = 23.1 Hz); 19.6 (d, ^2J(PCH) = 24.4 Hz). This spectrum corresponds to a mixture of compound **16** (24%) and **13** (76%).

Reaction of benzodioxaphosphole 20 with 4-nitrophenylacetylene. A solution of 4-nitrophenylacetylene (1.00 g, 6.8 mmol) and hex-1-ene (0.77 mL, 6.18 mmol) in CH_2Cl_2 (1 mL) was added dropwise to a solution of phosphorane **20** (2.2 g, 6.2 mmol), which was prepared from 3,6-di(*tert*-butyl)-1,2-benzoquinone (1.36 g) and phosphorus trichloride (1.1 mL), in CH_2Cl_2 (8 mL). The solvent and volatile products were removed from the reaction mixture in a vacuum of 12 Torr (the external-heating temperature was 100 °C), and the glassy pale-yellow compound, **5,8-di(*tert*-butyl)-2,6-dichloro-4-(4-nitrophenyl)-benzo[*e*]-1,2-oxaphosphinine 2-oxide (22)**, was obtained and characterized by spectroscopic methods. MS, *m*/*z* (I_{rel} (%)): 467 [M]$^{+\cdot}$ (2.2) ($C_{24}H_{24}Cl_2{}^{35}NO_4P$), 452 [M – Me]$^+$ (2.2), 411 [M – C_4H_8]$^+$ (16.2), 269 [$C_{14}H_7O_3N$]$^+$ (100). ^{1}H NMR ($CDCl_3$), δ: 1.12 (s, Bu^{t}C(8)); 1.42 (s, Bu^{t}C(5)); 6.53 (d, H(3), ^2J(PC(3)H) = 27.8 Hz); 7.29 (br.s, C(10)H, AA´ part of AA´XX´ system, ^3J(HCCH) = 7.6 Hz); 7.44 (d, H(7), ^5J(POCCC(7)H = 1.3 Hz); 8.18 (br.d, H(11), XX´ part of AA´XX´ system, ^3J(HCCH) = = 7.6 Hz). ^{13}C NMR ($CDCl_3$), δ$_C$: 117.10 (dd (d), C(3), ^1J(PC(3)) = 165.0 Hz, ^1J(HC(3)) = 172.6 Hz); 157.05 (m (d), C(4), ^2J(PCC(4)) = 2.4 Hz); 125.01 (ddm (d), C(4a), ^3J(PCCC(4a)) = = 20.0 Hz, ^3J(HC(3)CC(4a)) = 8.0 Hz); 147.24 (ddm (d), C(5), ^3J(HC(7)CC(5)) = 4.7 Hz, ^4J(PCCCC(5)) = 1.4 Hz); 131.70 (dd (d), C(6), ^2J(HC(7)C(6)) = 4.2 Hz, ^5J(PCCCCC(6)) = = 2.0 Hz); 133.00 (d (s), C(7), ^1J(HC(7)) = 165.6 Hz); 138.25 (ddm (d), C(8), ^3J(POCC(8)) = 6.8 Hz, ^2J(HC(7)C(8)) = = 3.6 Hz); 147.50 (dd (d), C(8a), ^3J(HC(7)CC(8a)) = 11.7 Hz, ^2J(POC(8a)) = 11.6 Hz); 148.16 (dtd (d), C(9), ^3J(PCCC(9)) = = 20.9 Hz, ^3J(HC(11)CC(9)) = 7.5 Hz, ^3J(HC(3)CC(9)) = = 6.0 Hz); 124.00 (dm (br.s), C(10), ^1J(HC(10)) = 171.6 Hz); 128.84 (dm (s), C(11), ^1J(HC(11)) = 164.2 Hz); 148.31 (tt (s), C(12), ^3J(HC(10)CC(12)) = 9.0 Hz, ^2J(HC(11)C(12)) = 3.0 Hz); 39.38 (m (s), C(15), ^2J(HC(16)C(15)) = 3.4 Hz); 30.26 (qqq (s), C(16), ^1J(HC(16)) = 126.9 Hz, ^3J(HCCC(16)) = 4.5 Hz); 34.90 (m (s), C(19), ^2J(HC(20)C(19)) = 3.5 Hz); 29.60 (qqq (s), C(20), ^1J(HC(20)) = 126.7 Hz, ^3J(HCCC(20)) = 4.6 Hz). ^{31}P NMR (CH_2Cl_2, 36.48 MHz), δ$_P$: 15.27 (d, ^2J(PCH) = 27.8 Hz).

2-[2,5-Di(*tert*-butyl)-4-chloro-2-hydroxyphenyl]-2-(4-nitrophenyl)vinylphosphonic acid (24) (1 : 1 acetone solvate). A 20 : 1 mixture of acetone and water (20 mL) was added to a mixture of phosphine **22** (2.9 g, 5.9 mmol). The crystalline precipitate that formed overnight was filtered off and washed with diethyl ether (5×4 mL). Yield 2.1 g (66%), m.p. 164 °C. Found (%): C, 54.97; H, 6.04; Cl, 6.87; N, 2.75; P, 6.58. $C_{25}H_{33}ClNO_7P$. Calculated (%): C, 57.09; H, 6.32; Cl, 6.74; N, 2.66; P, 5.89. IR (KBr), ν/cm^{-1}: 451, 492, 534, 553, 603, 682, 689, 703, 740, 762, 789, 820, 850, 858, 871, 890, 928, 947, 1000, 1092, 1112, 1178, 1254, 1342, 1362, 1425, 1486, 1521, 1577, 1687, 2341, 2360, 2872, 2961, 3021, 3536. ^{1}H NMR (DMSO-d$_6$), δ: 1.32 (s, Bu^{t}C(8)); 1.35 (s, Bu^{t}C(5)); 2.08 (s, 2 Me); 6.88 (d, H(3), ^2J(PC(3)H = 13.5 Hz); 7.25 (s, H(7)); 7.31 (br.d, H(10), AA´ part of AA´XX´ system, ^3J(HCCH) = 8.8 Hz); 8.17 (br.d, H(11), XX´ part of AA´XX´ system, ^3J(HCCH) = 8.8 Hz). ^{13}C NMR (DMSO-d$_6$), δ$_C$: 125.95 (dd (d), C(3), ^1J(PC(3)) = 184.9 Hz, ^1J(HC(3)) = 152.2 Hz); 150.97 (ddt (d), C(4), ^2J(PCC(4)) = 4.8 Hz, ^2J(HC1C(4)) = = 5.2 Hz, ^3J(HC(10)CC(4)) = 4.2 Hz); 130.10 (ddd (d), C(4a), ^3J(PCCC(4a)) = 7.0 Hz, ^3J(HC(3)CC(4a)) = 10.0 Hz, ^4J(HC(7)CCC(4a)) = 0.8 Hz); 151.86 (dd (d), C(8a), ^4J(PCCCC(8a)) = 2.2 Hz, ^3J(HC(7)CC(8a)) = 9.5 Hz); 138.88 (m (s), C(8), ^2J(HC(7)C(8)) = 3.5 Hz); 131.15 (d (s), C(7), ^1J(HC(7)) = 161.4 Hz); 126.74 (d (s), C(6), ^2J(HC(7)C(6)) = = 3.7 Hz); 142.29 (m (s), C(5)); 147.56 (dtd (d), C(9), ^3J(PCCC(9)) = 21.6 Hz, ^2J(HC(3)C(9)) = 6.5 Hz, ^3J(HC(11)CC(9)) = 6.5 Hz); 124.64 (dd (s), C(10), ^1J(HC(10)) = 171.7 Hz, ^2J(HC(11)C(10)) = 3.7 Hz); 127.70 (dd (s), C(11), ^1J(HC(11)) = 170.4 Hz, ^2J(HC(10)C(11)) = 6.2 Hz); 147.59 (tt (s), C(12), ^3J(HC(10)CC(12)) = 9.5 Hz, ^2J(HC(11)C(12)) = = 3.3 Hz); 34.64 (m (s), C(19), ^2J(HC(20)C(19)) = 3.6—4.0 Hz, ^3J(HC(7)CC(19)) = 3.6 Hz); 29.73 (qm (s), C(20), ^1J(HC(20)) = = 125.4 Hz); 206.75 (m (s), C(O), acetone, ^2J(HCC) = 5.9 Hz); 30.96 (m (s), Me, acetone, ^1J(HC) = 127.2 Hz, ^3J(HCC) = 1.5 Hz). ^{31}P NMR (DMSO-d$_6$), δ$_P$: 12.0 (d, ^2J(PCH) = 13.5 Hz).

Triethylammonium 2-[2,5-di(*tert*-butyl)-4-chloro-2-hydroxyphenyl]-2-(4-nitrophenyl)vinylphosphonate (25). Triethylamine (0.077 mL, 0.52 mmol) was added to a solution of phosphonic acid **24** (as the 1 : 1 acetone solvate) (0.14 g, 0.26 mmol) in diethyl ether (5 mL). The reaction mixture was stirred for 3 h. The white precipitate that formed was filtered off and washed with diethyl ether (5×1 mL). Yield 0.14 g (97%), m.p. 189 °C. Found (%): C, 58.03; H, 8.11; Cl, 6.02; N, 4.97; P, 5.74.

$C_{28}H_{42}ClN_2O_6P$. Calculated (%): C, 59.10; H, 7.44; Cl, 6.23; N, 4.92; P, 5.44. IR (KBr), ν/cm^{-1}: 459, 580, 624, 763, 798, 853, 1024, 1086, 1135, 1177, 1229, 1252, 1294, 1326, 1396, 1441, 1462, 1502, 1589, 2047, 2837, 2907, 2934, 2955, 3002, 3081. ^{1}H NMR (DMSO-d_6), δ: 0.87 (t, NCMe, ^3J(HCCH) = 7.3 Hz); 1.30 (s, Bu^{t}C(8)); 1.36 (s, Bu^{t}C(5)); 2.01 (br.q, NH, ^3J(HCCH) = = 7.3 Hz); 6.77 (d, H(3), ^2J(PC(3)H) = 11.0 Hz); 7.05 (d.br.d, C(10)H, AA´ part of AA´XX´ system, ^3J(HCCH) = 9.0 Hz); 7.15 (s, H(7)); 8.08 (d.br.d, C(11)H, XX´ part of AA´XX´ system, ^3J(HCCH) = 9.0 Hz). ^{13}C NMR (DMSO-d_6), δ_C: 131.17 (dd (d), C(3), ^1J(PC(3)) = 172.0 Hz, ^1J(HC(3)) = 147.5 Hz); 147.48 (ddt (d), C(4), ^2J(PCC(4)) = 4.4 Hz, ^2J(HC(3)C(4)) = 4.8 Hz, ^3J(HC(10)CC(4)) = 3.9 Hz); 132.30 (dd (d), C(4a), ^3J(PCCC(4a)) = 5.9 Hz, ^3J(HC(3)CC(4a)) = 3.9 Hz); 152.83 (dd (d), C(8a), ^4J(PCCCC(8a)) = 1.7 Hz, ^3J(HC(7)CC(8a)) = = 9.5 Hz); 139.54 (m (s), C(8)); 130.31 (d (s), C(7), ^1J(HC(7)) = = 161.0 Hz); 126.65 (d (s), C(6), ^2J(HC(7)C(6)) = 3.7 Hz); 142.46 (m (s), C(5)); 149.84 (dtd (d), C(9), ^3J(PCCC(9)) = 19.8 Hz, ^2J(HC(11)C(9)) = 5.9 Hz, ^3J(HC(3)CC(9)) = 5.9 Hz); 123.61 (dd (s), C(10), ^1J(HC(10)) = 165.1 Hz, ^2J(HC(11)C(10)) = 3.7 Hz); 127.07 (dd (s), C(11), ^1J(HC(11)) = 163.6 Hz, ^2J(HC(10)C(11)) = 6.6 Hz); 146.73 (tm (s), C(12), ^3J(HC(10)CC(12)) = 9.5 Hz); 38.37 (m (s), C(15)); 31.23 (qm (s), C(16), ^1J(HC(16)) = 126.3 Hz); 34.65 (m (s), C(19)); 29.84 (qm (s), C(20), ^1J(HC(20)) = = 126.9 Hz); 45.77 (br.t (s), CH_2 (NEt), ^1J(HC) = 143.8 Hz); 8.69 (q (s), Me (NEt), ^1J(HC) = 128.0 Hz). ^{31}P NMR (DMSO-d_6) δ_P: 9.6 (d, ^2J(PCH) = 11.0 Hz).

Reaction of benzodioxaphosphole 20 with 4-methoxyphenylacetylene. A solution of 4-methoxyphenylacetylene (1.26 g, 9.6 mmol) and hex-1-ene (1.1 mL, 8.8 mmol) in CH_2Cl_2 (5 mL) was added to a solution of phosphorane **20** (3.1 g, 8.7 mmol), which was prepared from 3,6-di(*tert*-butyl)-1,2-benzoquinone (1.91 g) and phosphorus trichloride (3.1 mL), in CH_2Cl_2 (20 mL). The solvent and volatile products were removed from the reaction mixture in a vacuum of 12 Torr (the external-heating temperature was 100 °C), and pentane (15 mL) was added to the glassy pale-yellow residue. The white crystalline precipitate of **5,8-di(*tert*-butyl)-2,6-dichloro-4-(4-methoxyphenyl)benzo[*e*]-1,2-oxaphosphinine 2-oxide (26)** that formed overnight was filtered off under argon and washed with a cold (0—−5 °C) 10 : 1 pentane—CH_2Cl_2 mixture (3×5 mL). Yield 3.2 g (82%), m.p. 111—113 °C. MS, m/z (I_{rel} (%): 452 $[M]^{+\cdot}$ (2.2) ($C_{23}H_{27}Cl_2{}^{35}O_3P$), 437 $[M - Me]^+$ (3.5), 417 $[M - Cl]^+$ (2.0), 396 $[M - C_4H_8]^+$ (75.9), 381 $[M - C_4H_8 - Me]^+$ (30.3), 365 $[M - C_4H_8 - OMe]^+$ (100.0). ^{1}H NMR ($CDCl_3$), δ: 1.18 (s, Bu^{t}C(8)); 1.36 (s, Bu^{t}C(5)); 6.30 (d, H(3), ^2J(PC(3)H = 27.7 Hz); 6.83 (br.s, H(10), AA´ part of AA´XX´ system); 6.98 (br.s, C(11)H, XX´ part of AA´XX´ system); 7.42 (d, H(7), ^5J(POCCC(7)H = 1.4 Hz). ^{13}C NMR ($CDCl_3$), δ_C: 55.406 (q (s), OMe, ^1J(HC) = 144.3 Hz); 112.64 (dd (d), C(3), ^1J(PC(3) Hz) = 164.2, ^1J(HC(3)) = 171.6 Hz); 159.67 (m (d), C(4), ^2J(PCC(4)) = 2.4 Hz); 126.28 (ddd (d), C(4a), ^3J(PCCC(4a)) = 20.3 Hz, ^3J(HC(3)CC(4a)) = = 16.6 Hz, ^4J(HC(7)CCC(4a)) = 1.0 Hz); 147.89 (m (d), C(5), ^4J(PCCCC(5)) = 1.4 Hz); 131.19 (m (d), C(6), ^5J(PCCCCC(6)) = = 2.0 Hz); 132.22 (d (s), C(7), ^1J(HC(7)) = 165.0 Hz); 137.68 (m (d), C(8), ^3J(POCC(8)) = 6.8 Hz); 147.51 (m (d), C(8a), ^2J(POC(8a)) = 11.3 Hz); 134.77 (dm (d), C(9), ^3J(PCCC(9)) = = 20.8 Hz); 129.38 (m (s), C(10), ^1J(HC(10)) = 166.7 Hz); 114.25 (dm (s), C(11), ^1J(HC(11)) = 161.1 Hz); 159.51 (m (s), C(12)); 39.70 (m (s), C(15), ^2J(HC(16)C(15)) = 3.6 Hz); 29.75 (q.sept (s), C(16), ^1J(HC(16)) = 126.7 Hz, ^3J(HCCC(16)) = = 4.7 Hz); 34.85 (d.dec (s), C(19), ^2J(HC(20)C(19)) = = 3.5 Hz); 29.43 (q.sept (s), C(20), ^1J(HC(20)) = 126.5 Hz, ^3J(HCCC(20)) = 4.8 Hz). ^{31}P NMR (DMSO-d_6), δ_P: 18.8 (d, ^2J(PCH) = 27.7 Hz).

2-[3,6-Di(*tert*-butyl)-5-chloro-2-hydroxy)-2-(4-methoxyphenyl)vinylphosphonic acid (29). A 20 : 1 acetone—water mixture (20 mL) was added to phosphine **26** (0.6 g, 1.3 mmol). The white precipitate of compound **29** that formed was filtered off and washed with diethyl ether (3×4 mL). Yield 0.48 g (80%), m.p. 188—190 °C. Found (%): C, 58.87; H, 7.01; Cl, 7.78; P, 6.92. $C_{23}H_{30}ClO_5P$. Calculated (%): C, 60.99; H, 6.68; Cl, 7.83; P, 6.84. IR (KBr), ν/cm^{-1}: 470, 491, 513, 526, 546, 568, 621, 640, 695, 718, 754, 811, 858, 912, 1038, 1075, 1113, 1178, 1215, 1254, 1284, 1308, 1367, 1473, 1509, 1595, 2325, 2624, 2678, 2953, 3411. ^{1}H NMR (DMSO-d_6), δ: 1.35 (s, Bu^{t}C(8)); 1.37 (s, Bu^{t}C(5)); 6.49 (d, H(3), ^2J(PC(3)H = 12.7 Hz); 6.84 (br.m, H(11), AA´ part of AA´XX´ spectrum); 6.89 (br.m, H(10), XX´ part of AA´XX´ spectrum); 7.17 (br.s, H(7)). ^{31}P NMR (DMSO-d_6), δ_P: 10.8 (d, ^2J(PC(3)H) = 12.7 Hz).

2-*tert*-Butylamino-5,8-di(*tert*-butyl)-6-chloro-4-(4-methoxyphenyl)benzo[*e*]-1,2-oxaphosphinine 2-oxide (28). *tert*-Butylamine (1.4 mL, 13.2 mmol) was added to a solution of phosphine **26** (3.0 g, 6.6 mmol) in diethyl ether (30 mL) under an atmosphere of dry argon. The white precipitate of compound **28** and *tert*-butylammonium chloride that formed was washed with a 5% sodium hydrocarbonate solution (5×10 mL), water (2×10 mL), and diethyl ether (5×4 mL) and dried in vacuum of 12 Torr. Yield 2.4 g (75%), m.p. 239 °C. Found (%): C, 65.44; H, 7.97; Cl, 7.13; N, 2.93; P, 6.45. $C_{27}H_{37}ClNO_3P$. Calculated (%): C, 66.18; H, 7.61; Cl, 7.24; N, 2.86; P, 6.32. IR (Nujol mulls), ν/cm^{-1}: 425, 477, 557, 583, 629, 689, 722, 743, 779, 813, 836, 871, 959, 1019, 1037, 1084, 1134, 1179, 1199, 1237, 1313, 1369, 1415, 1453, 1509, 1544, 1580, 1607, 1743, 2342, 2360, 3247. ^{1}H NMR (DMSO-d_6—$CDCl_3$ (3 : 2)), δ: 1.11 (s, Bu^{t}C(8)); 1.34 (s, Bu^{t}C(5)); 1.42 (s, Bu^t(NH)); 5.20 (br.d, NH, ^2J(PNH) = 9.6 Hz); 6.10 (d, H(3), ^2J(PC(3)H = 23.7 Hz); 6.80 (br.m, H(10), AA´ part of AA´XX´ system); 6.93 (br.s, H(11), XX´ part of AA´XX´ system); 7.20 (s, H(7)). ^{31}P NMR (DMSO-d_6—$CDCl_3$ (3 : 2), 36.48 MHz), δ_P: 10.3 (dd, ^2J(PCH) = 23.6 Hz, ^2J(PNH) = 9.6 Hz).

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