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# Reactions of Phenylenedioxytrihalophosphoranes with Arylacetylenes: III.[1] Features of Reactions of 5,6-Dihalo-2-chlorobenzo[*d*]-1,3,2-dioxaphosphole 2,2-Dichloride with Arylacetylenes

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**Abstract**—According to the NMR, IR, and high-resolution mass spectra, the major products of the reactions of 5,6-dibromo-2-chlorobenzo[*d*]-1,3,2-dioxaphosphole 2,2-dichloride with arylacetylenes are 4-aryl-6,7-dibromo-2-chloro-5,6-benzo[*e*]-1,2-oxaphosphorin-3-ene 2-oxides. The steric structure of one of the hydrolysis products, 2-hydroxy-6,7-dibromo-4-phenyl-5,6-benzo[*e*]-1,2-oxaphosphorin-3-ene 2-oxide, was studied by single crystal X-ray diffraction.

We found previously that reactions of phenylenedioxytrichlorophosphorane (**I**) with arylacetylenes unexpectedly yield derivatives of benzo[*e*]-1,2-oxaphosphorin-3-ene, an organophosphorus analog of coumarin [2, 3]. The result of the reaction under mild conditions formally resembles that of the Arbuzov reaction: formation of the phosphoryl group and a P–C bond. However, the initial compound is a phosphorane, and the phosphoryl group is formed by *ipso* substitution of carbon for oxygen. The reaction also involves another unusual process: regioselective chlorination of the benzene ring at the *p*-position relative to the oxygen atom of the newly formed oxaphosphorine heteroring. When the benzo fragment of the initial phosphorane contains a halogen, derivatives of 6,7-dihalobenzo[*e*]-1,2-oxaphosphorin-3-ene are formed; in the product, the halogen atom initially present in the ring is at the *m*-position relative to the oxygen atom of the oxaphosphorine ring, and the second halogen atom migrating to the aromatic ring, at the *p*-position [1].

Here we report on the reaction of arylacetylenes with phenylenedioxytrichlorophosphoranes containing halogen atoms at the *p*-position relative to the oxygen atoms. We found that previously unknown 5,6-dibromo-2-chlorobenzo[*d*]-1,3,2-dioxaphosphole 2,2-dichloride (**II**) readily reacts with phenyl- and *p*-chlorophenylacetylenes to give, according to the $^{31}$P NMR data, two phosphorus-containing products in the ratio from 8 : 1 to 10 : 1. The two bromine atoms present in the benzene ring do not prevent the reaction.

From the reaction mixture, we distilled off a mixture of *cis*- and *trans*-dichlorostyrenes (see Experimental), which are probably formed by addition of a chlorine molecule released in the reaction to excess acetylene. The electron impact mass spectrum of the residue obtained after removal of volatiles contains peaks at *m*/*z* 432 and 388. The precisely measured weights of ions giving these peaks (431.8284 and 387.8729) are consistent with the formulas $C_{14}H_8Br_2ClO_2P$ (431.8317) and $C_{14}H_8BrCl_2O_2P$ (387.8822). Taking into account also the $^1$H (see Experimental) and $^{13}$C (Table 1[2]) NMR data, we identified these compounds as 6,7-dibromo-4-phenyl-2-chloro- and 7-bromo-4-phenyl-2,6-dichlorobenzo[*e*]-1,2-oxaphosphorin-3-ene 2-oxides **IIIa** and **IVa**.

The main fragmentation pathway of **IIIa** and **IVa** under electron impact involves cleavage of the P–Cl bond to give ions with *m*/*z* 397 and 353, respectively.

[1] For communication II, see [1].

[2] In the tables and hereinafter in the text, the atom numbering is arbitrary; it is shown in the structural formulas of **III**, **V**, **VIII**, and **IX**.

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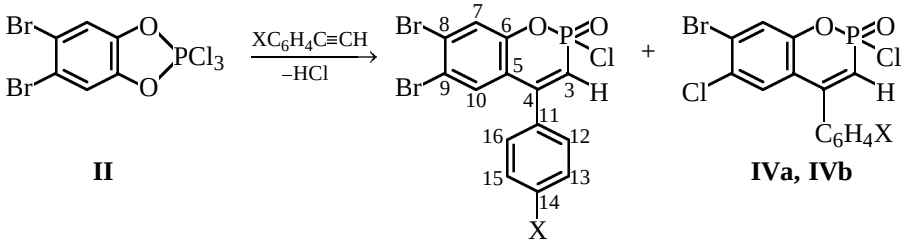


**II** **IVa, IVb**

**IIIa, IIIb**

X = H (**a**), 4-Cl (**b**).

The $^{13}$C NMR spectrum of **IIIa** contains four signals of *ipso*-C atoms, which suggests the presence of only two bromine atoms in the benzo substituent. Apparently, in this limiting case the third halogen atom is not incorporated. Another very interesting result of the reaction of **I** with arylacetylenes is partial occurrence of *ipso* substitution of chlorine for bromine at the *p*-position relative to the oxaphosphorinane oxygen atom. The structure of phosphorines **IV** was readily determined by comparison of the spectral parameters with those of compound **IVa** prepared previously [1]. In reactions of phosphorane **II** with phe-

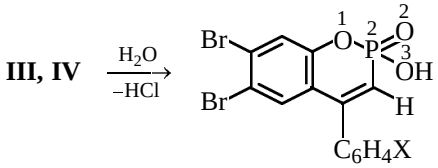
**Table 1.** $^{13}$C NMR spectra [δ, ppm (*J*, Hz)] of **III**, **V**, **IX**, and **XI** (100.6 MHz, 35°C)

| Atom | **IIIa** ($CDCl_3$) | **Va** (DMF-$d_7$) |
|---|---|---|
| $C^3$ | 115.92 d[a] (d.d)[b] (153.9, $PC^3$; 172.0, $HC^3$) | 117.31 d (d.d) (169.2, $PC^3$; 163.5, $HC^3$) |
| $C^4$ | 155.39 s (br.s) | 149.65 br.s (br.m) |
| $C^5$ | 122.54 d (d.d.d) (18.2, $PCCC^5$; 7.9–8.1, $HC^3CC^5$; 5.7–5.8, $HC^7CC^5$) | 123.16 d (d.d.d) (16.6, $PCCC^5$; 9.3, $HC^3CC^5$; 5.3–5.5, $HC^7CC^5$) |
| $C^6$ | 150.16 d (d.d.d) (10.6, $POC^6$; 9.8–10.1, $HC^{10}C^5C^6$; 5.0, $HC^7C^6$) | 150.59 d (m) (7.0, $POC^6$) |
| $C^7$ | 125.21 d (d.d) (171.8, $HC^7$; 8.2, $POCC^7$) | 123.83 d (d.d) (169.9, $HC^7$; 6.1, $POCC^7$) |
| $C^8$ | 128.74 s (d.d) (9.9, $HC^{10}CC^8$; 4.4, $HC^7C^8$) | 124.73 s (d.d) (10.5, $HC^{10}CC^8$; 4.2, $HC^7C^8$) |
| $C^9$ | 121.28 br.s (br.d.d) (8.7, $HC^7CC^9$; 4.2, $HC^{10}C^9$) | 116.94 s (d.d) (8.5, $HC^7CC^9$; 4.0, $HC^{10}C^9$) |
| $C^{10}$ | 134.01 s (d) (169.6, $HC^{10}$) | 131.81 s (d) (167.7, $HC^{10}$) |
| $C^{11}$ | 136.63 d (d.t.d) (20.6, $PCCC^{11}$; 7.1, $HC^{13}CC^{11}$; 6.5, $HC^3CC^{11}$) | 137.46 d (d.t.d) (18.2, $PCCC^{11}$; 7.2–7.4, $HC^{13}CC^{11}$; 5.0–6.0, $HC^3CC^{11}$) |
| $C^{12}$, $C^{16}$ | 128.63 s (d.d) (163.1, $HC^{12}$; 6.7, $HC^{16}CC^{12}$; 5.7, $HC^{14}CC^{12}$) | 127.81 s (d.d.d) (160.4, $HC^{12}$; 6.6, $HC^{16}CC^{12}$; 6.0, $HC^{14}CC^{12}$) |
| $C^{13}$, $C^{15}$ | 129.63 s (d.d) (163.1, $HC^{13}$; 6.5, $HC^{15}CC^{13}$) | 128.24 s (d.d) (161.5, $HC^{13}$; 6.5, $HC^{15}CC^{13}$) |
| $C^{14}$ | 130.77 s (d.t) (162.1, $HC^{14}$; 7.2, $HC^{12,16}CC^{14}$) | 128.55 s (d.t) (161.6, $HC^{14}$; 7.3, $HC^{12,16}CC^{14}$) |
| Atom | **IX** ($CDCl_3$) | **XI** (DMF-$d_7$) |
| $C^3$ | 115.47 d (153.5, $PC^3$) | 117.21 d (d.d) (169.5, $PC^3$; 163.6, $HC^3$) |
| $C^4$ | 154.96 d (1.1, $PCC^4$) | 150.14 s (br.m) |
| $C^5$ | 121.78 d (18.4, $PCCC^5$) | 122.70 d (m) (16.6, $PCCC^5$) |
| $C^6$ | 149.43 d (9.7, $POC^6$) | 150.47 d (m) (6.9, $POC^6$) |
| $C^7$ | 121.61 d (8.8, $POCC^7$) | 121.09 d (d.d) (170.0, $HC^7$; 7.3, $POCC^7$) |
| $C^8$ | 137.96 s | 134.77 s (m) |
| $C^9$ | 118.47 s | 114.18 s (m) |
| $C^{10}$ | 133.89 s | 132.33 s (d) (167.0, $HC^{10}$) |
| $C^{11}$ | 136.27 d (20.5, $PCCC^{11}$) | 137.76 d (m) (18.2, $PCCC^{11}$) |
| $C^{12}$, $C^{16}$ | 128.38 s | 128.09 s (d.m) (160.5–161.0, $HC^{12}$) |
| $C^{13}$, $C^{15}$ | 129.27 s | 128.54 s (d.m) (160.7–161.3, $HC^{13}$) |
| $C^{14}$ | 130.44 s | 128.86 s (d.t) (161.4, $HC^{14}$; 7.3, $HC^{12,16}CC^{14}$) |

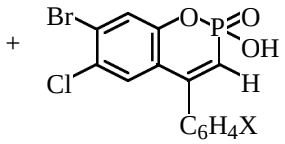
[a] With proton decoupling. [b] Without proton decoupling.

nylacetylene, the ratio of products **IIIa** and **IVa** depends on the concentration of the reactants in the initial solution. As the concentration of the initial phosphorane is decreased in the series 1.44, 0.72, 0.48, 0.36, 0.288, and 0.07 M (at a constant reactant ratio of 1 : 2), the ratio of **IIIa** and **IVa** varies, respectively, as follows: 79.0 : 21.0, 77.6 : 22.4, 73.2 : 26.8, 73.2 : 26.8, 72.7 : 27.3, 71.6 : 28.4, and 63.3 : 36.7, i.e., the relative content of the *ipso* substitution product **IVa** slightly increases, probably owing to increased contribution of the intramolecular mechanism of chlorine migration. It should be noted also that dibromo-substituted phosphorane **II** and unsubstituted phenylenedioxytrichlorophosphorane **I** show a similar reactivity in concurrent reaction with phenylacetylene.

Hydrolysis of **IIIa**, **IIIb**, **IVa**, and **IVb** in dioxane gave the corresponding phosphonic acids **Va**, **Vb**, **VIa**, and **VIb**. The major products **Va** and **Vb** were isolated by fractional crystallization.




**Va, Vb**




**VIa, VIb**

The structure of **V** and **VI** was determined by $^{1}H$, $^{31}P$, and $^{13}C$ NMR and IR spectroscopy (see Experimental; Table 1) and by comparison with the spectral parameters of a sample of **VIa** prepared by independent synthesis [1] (the mass spectrum of this compound is discussed in the Experimental).

Data in Table 1 suggest that hydrolysis lefts intact the phosphorine ring. This conclusion is confirmed by the single crystal X-ray diffraction data for **Va**. The atomic coordinates for the dioxane solvate of **Va** and the selected bond lengths, bond angles, and torsion angles are listed in Tables 2 and 3. The steric structure of the complex of **Va** with dioxane in the crystal is shown in Fig. 1. It is seen that the acid molecule is cyclic, with the positions of both bromine atoms preserved. The phosphorine ring has the distorted *boat* conformation: The $O^1C^6C^5C^4$ fragment is planar within 0.01(1) Å, and the $P^2$ and $C^3$ atoms deviate in the same direction by –0.596(3) and –0.237(11) Å, respectively. The phosphoryl group

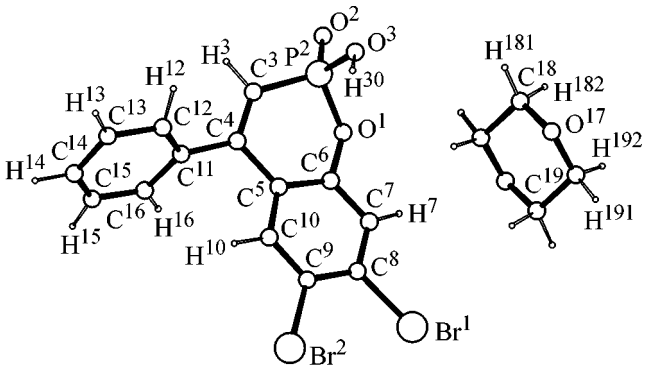



**Fig. 1.** Structure of the complex of benzophosphorine **Va** with dioxane in the crystal.

occupies the equatorial position [the $O^2$ atom deviates from the $O^1C^6C^5C^4$ plane by 0.026(8) Å], and the hydroxy group, the axial position [the $O^3$ atom deviates from the $O^1C^6C^5C^4$ plane by –2.119(8) Å], which is consistent with the anomeric effect of $O^3$. The $P^2$–$O^3$ bond is somewhat longer [1.544(8) Å] as compared to the related 2-hydroxy-4-phenyl-6,7-dichlorobenzo[*e*]-1,2-oxaphosphorin-3-ene 2-oxide (**VII**) [1.525(5) Å] and **VIa** [1.519(3) Å] [1], which are isostructural. Similar to **VIa** and **VII**, this is due to realization of the conformation favorable for interaction of the π system of the $C^3$=$C^4$ bond with the $P^2$–$O^3$ antibonding orbital [$\tau(O^3P^2C^3C^4)$ 92(1)°]. The length of the endocyclic $P^2$–$O^1$ bond [1.593(9) Å] coincides within the limits of the experimental error with the corresponding bond lengths in **VIa** and **VII** [1.596(5) and 1.590(4) Å, respectively] [1].

The phenyl substituent is turned relative to the dibromophenylene ring plane by an angle as large as 63(2)° [$\tau(C^5C^4C^{11}C^{16})$], which rules out any conjugation between them. The heterocyclic moiety contains another planar [within 0.01(1) Å] fragment, $P^2C^3C^4C^5$, from which the $C^6$ and $O^1$ atoms deviate in the same direction by 0.244(11) and 0.529(9) Å, respectively. The $O^2$ and $O^3$ atoms deviate from the $P^2C^3C^4C^5$ ring in different directions by 0.870(8)–1.447(7) Å. The planar fragments are turned relative to each other about the $C^4$–$C^5$ bond by 13(2)°. The solvent (dioxane) molecule has a usual *chair* conformation; the distances between the dioxane and benzophosphorine molecules correspond to van der Waals contacts.

Figure 2 shows the system of hydrogen bonds in the crystal of the complex of **Va** with dioxane. The benzophosphorine molecules form an infinite chain of intermolecular hydrogen bonds $O^3$–$H^{30}\cdots O^{2'}$ = $P(x-1, y, z)$, directed along the *x*-axis, with the parameters $O^3$–$H^{30}$ 1.08, $O^{2'}\cdots H^{30}$ 1.43, $O^3\cdots O^{2'}$ 2.475(10) Å, angle $O^3$–$H^{30}\cdots O^{2'}$ 160°.

**Table 2.** Atomic coordinates, equivalent isotropic temperature factors of nonhydrogen atoms $\left[B = 4/3\sum_{i=1}^{3}\sum_{j=1}^{3}(a_i a_j)B(i,j)\ (\text{Å}^2)\right]$, and isotropic temperature factors of hydrogen atoms $B_{iso}$ (Å$^2$) for **Va**

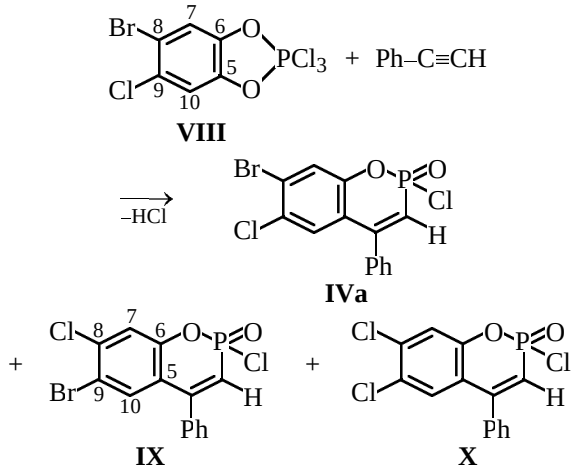
| Atom | *x* | *y* | *z* | *B* or $B_{iso}$ | Atom | *x* | *y* | *z* | *B* or $B_{iso}$ |
|---|---|---|---|---|---|---|---|---|---|
| $Br^1$ | 1.0194(4) | 0.0936(1) | 0.6559(1) | 4.68(4) | $C^{14}$ | 0.498(3) | 0.856(1) | 0.628(1) | 4.7(4) |
| $Br^2$ | 1.1632(4) | 0.3486(2) | 0.5568(1) | 4.87(4) | $C^{15}$ | 0.383(3) | 0.781(1) | 0.5891(9) | 3.6(4) |
| $P^2$ | 0.1938(7) | 0.3949(3) | 0.9169(2) | 2.01(8) | $C^{16}$ | 0.355(3) | 0.676(1) | 0.6340(9) | 2.7(3) |
| $O^1$ | 0.280(2) | 0.3057(7) | 0.8479(5) | 2.4(2) | $C^{18}$ | 0.795(3) | 0.087(1) | 0.979(1) | 5.9(5) |
| $O^2$ | –0.095(2) | 0.3811(7) | 0.9517(6) | 2.7(2) | $C^{19}$ | 1.099(4) | –0.051(1) | 0.928(1) | 6.5(5) |
| $O^3$ | 0.406(1) | 0.3677(7) | 0.9950(5) | 2.3(2) | $H^3$ | 0.1447 | 0.5903 | 0.8712 | 1 |
| $O^{17}$ | 0.815(2) | 0.0014(9) | 0.9282(7) | 5.6(3) | $H^7$ | 0.5020 | 0.1498 | 0.7770 | 6 |
| $C^3$ | 0.243(2) | 0.522(1) | 0.8497(8) | 1.5(3) | $H^{10}$ | 0.8118 | 0.5064 | 0.6522 | 2 |
| $C^4$ | 0.402(2) | 0.534(1) | 0.7770(8) | 1.8(3) | $H^{12}$ | 0.5439 | 0.7301 | 0.8315 | 6 |
| $C^5$ | 0.547(2) | 0.428(1) | 0.7457(7) | 1.6(3) | $H^{13}$ | 0.6674 | 0.8866 | 0.7535 | 5 |
| $C^6$ | 0.486(2) | 0.318(1) | 0.7837(8) | 1.9(3) | $H^{14}$ | 0.5321 | 0.9351 | 0.5948 | 6 |
| $C^7$ | 0.625(2) | 0.220(1) | 0.7568(8) | 2.0(3) | $H^{15}$ | 0.2890 | 0.7849 | 0.5236 | 6 |
| $C^8$ | 0.832(2) | 0.231(1) | 0.6903(8) | 2.0(3) | $H^{16}$ | 0.2883 | 0.6229 | 0.6073 | 6 |
| $C^9$ | 0.894(2) | 0.335(1) | 0.6499(8) | 2.0(3) | $H^{181}$ | 0.6038 | 0.1231 | 0.9871 | 8 |
| $C^{10}$ | 0.757(2) | 0.432(1) | 0.6798(8) | 1.7(3) | $H^{182}$ | 0.9056 | 0.1488 | 0.9582 | 8 |
| $C^{11}$ | 0.442(2) | 0.644(1) | 0.7239(9) | 2.2(3) | $H^{191}$ | 1.1243 | –0.1094 | 0.8870 | 7 |
| $C^{12}$ | 0.559(3) | 0.720(1) | 0.7648(9) | 3.5(4) | $H^{192}$ | 1.2282 | 0.0048 | 0.9012 | 7 |
| $C^{13}$ | 0.589(3) | 0.831(1) | 0.718(1) | 4.7(4) | $H^{30}$ | 0.3795 | 0.6133 | 1.0150 | 4 |

**Table 3.** Selected bond lengths (*d*, Å), bond angles (φ, deg), and torsion angles (τ, deg) in the molecule of **Va**

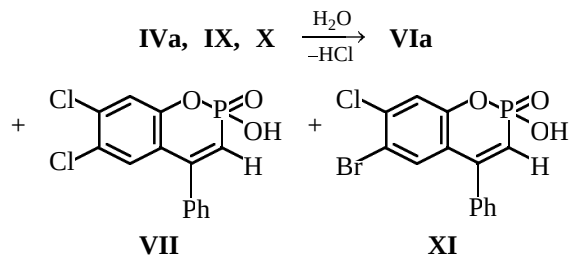
| Bond | *d* | Bond | *d* | Angle | φ | Angle | φ |
|---|---|---|---|---|---|---|---|
| $Br^1$–$C^8$ | 1.89(1) | $C^8$–$C^9$ | 1.37(2) | $O^1P^2O^2$ | 108.7(5) | $O^1C^6C^5$ | 120(1) |
| $Br^2$–$C^9$ | 1.87(1) | $C^9$–$C^{10}$ | 1.38(2) | $O^1P^2O^3$ | 107.4(4) | $O^1C^6C^7$ | 117(1) |
| $P^2$–$O^1$ | 1.593(9) | $C^{10}$–$H^{10}$ | 0.98(1) | $O^1P^2C^3$ | 100.9(5) | $C^5C^6C^7$ | 122(1) |
| $P^2$–$O^2$ | 1.483(8) | $C^{11}$–$C^{12}$ | 1.35(2) | $O^2P^2O^3$ | 110.4(5) | $C^6C^7C^8$ | 118(1) |
| $P^2$–$O^3$ | 1.544(8) | $C^{11}$–$C^{16}$ | 1.40(2) | $O^2P^2C^3$ | 117.3(5) | $C^6C^7H^7$ | 109(1) |
| $P^2$–$C^3$ | 1.73(1) | $C^{12}$–$C^{13}$ | 1.42(2) | $O^3P^2C^3$ | 111.2(5) | $C^{14}C^{15}C^{16}$ | 121(1) |
| $O^1$–$C^6$ | 1.36(1) | $C^{12}$–$H^{12}$ | 1.02(1) | $P^2O^1C^6$ | 123.4(8) | $C^{11}C^{16}C^{15}$ | 122(1) |
| $O^{17}$–$C^{18}$ | 1.34(2) | $C^{13}$–$C^{14}$ | 1.40(2) | $C^{18}O^{17}C^{19}$ | 109(1) | $Br^1C^8C^7$ | 116.9(8) |
| $O^{17}$–$C^{19}$ | 1.43(2) | $C^{13}$–$H^{13}$ | 1.02(2) | $P^2C^3C^4$ | 126.4(9) | $Br^1C^8C^9$ | 121.4(9) |
| $C^3$–$C^4$ | 1.31(2) | $C^{14}$–$C^{15}$ | 1.32(2) | $P^2C^3H^3$ | 114.6(9) | $Br^2C^9C^8$ | 121.3(9) |
| $C^3$–$H^3$ | 0.98(1) | $C^{14}$–$H^{14}$ | 1.03(1) | $C^4C^3H^3$ | 119(1) | $Br^2C^9C^{10}$ | 119.8(9) |
| $C^4$–$C^5$ | 1.48(2) | $C^{15}$–$C^{16}$ | 1.35(2) | $C^3C^4C^5$ | 118(1) | $C^5C^{10}C^9$ | 122(1) |
| $C^4$–$C^{11}$ | 1.46(2) | $C^{15}$–$H^{15}$ | 1.08(1) | $C^3C^4C^{11}$ | 124(1) | $C^5C^{10}H^{10}$ | 120(1) |
| $C^5$–$C^6$ | 1.42(2) | $C^{16}$–$H^{16}$ | 0.89(1) | $C^5C^4C^{11}$ | 118(1) | $C^9C^{10}H^{10}$ | 118(1) |
| $C^5$–$C^{10}$ | 1.38(2) | $C^{18}$–$H^{181}$ | 0.98(2) | $C^4C^5C^6$ | 122(1) | $C^4C^{11}C^{12}$ | 118(1) |
| $C^6$–$C^7$ | 1.37(2) | $C^{18}$–$H^{182}$ | 0.97(2) | $C^4C^5C^{10}$ | 122(1) | $C^4C^{11}C^{16}$ | 124(1) |
| $C^7$–$C^8$ | 1.38(2) | $C^{19}$–$H^{191}$ | 0.98(2) | $C^6C^5C^{10}$ | 116(1) | $C^{12}C^{11}C^{16}$ | 118(1) |
| $C^7$–$H^7$ | 1.09(1) | $C^{19}$–$H^{192}$ | 1.00(2) | | | | |

| Angle | τ | Angle | τ | Angle | τ | Angle | τ |
|---|---|---|---|---|---|---|---|
| $O^2P^2O^1C^6$ | 158.67(0.85) | $C^{11}C^4C^5C^{10}$ | 12.60(1.64) | $O^3P^2C^3C^4$ | 91.82(1.14) | $C^5C^6C^7H^7$ | –161.30(1.03) |
| $O^3P^2O^1C^6$ | –81.85(0.92) | $C^3C^4C^{11}C^{12}$ | 61.58(1.71) | $O^3P^2C^3H^3$ | –85.45(0.96) | $H^7C^7C^8Br^1$ | –23.27(1.76) |
| $C^3P^2O^1C^6$ | 34.69(0.96) | $C^3C^4C^{11}C^{16}$ | –115.43(1.45) | $P^2O^1C^6C^5$ | –29.31(1.44) | $H^7C^7C^8C^9$ | 155.56(1.22) |
| $O^1P^2C^3C^4$ | –21.90(1.18) | $C^5C^4C^{11}C^{12}$ | –119.51(1.29) | $P^2O^1C^6C^7$ | 152.01(0.89) | $C^4C^{11}C^{12}H^{12}$ | –30.23(2.12) |
| $O^1P^2C^3H^3$ | 160.83(0.86) | $C^5C^4C^{11}C^{16}$ | 63.47(1.60) | $C^3C^4C^5C^6$ | 9.41(1.67) | $C^{16}C^{11}C^{12}H^{12}$ | 146.96(1.43) |
| $O^2P^2C^3C^4$ | –139.80(1.04) | $C^4C^5C^6O^1$ | 3.14(1.66) | $C^3C^4C^5C^{10}$ | –168.42(1.11) | $H^{12}C^{12}C^{13}C^{14}$ | –153.79(1.36) |
| $O^2P^2C^3H^3$ | 42.92(1.11) | $O^1C^6C^7H^7$ | 17.35(1.50) | $C^{11}C^4C^5C^6$ | –169.57(1.07) | $H^{12}C^{12}C^{13}H^{13}$ | 23.76(1.91) |

The most interesting was the reaction pattern in the case of disubstituted trichlorophosphorane **VIII** containing two different halogen atoms, chlorine and bromine, in the phenylene ring. We obtained three chlorophosphorines **IVa**, **IX**, and **X** in a ~3 : 5 : 2 ratio.




The structure of **IVa** and **X** was determined by comparison of the $^{13}C$ NMR spectra of the reaction mixture with those of authentic samples of **IVa** and **X**, prepared and discussed in detail previously [1]. Hydrolysis of the reaction mixture gave phosphonic acids **VIa**, **VII**, and **XI**. We failed to isolate the individual acids by the subsequent fractional crystallization of the precipitate and obtained only fractions rich in one or another product. Table 1 gives the $^{13}C$ NMR data for phosphorine **IX** and phosphonic acid **XI**. Since the orientation of the halogen atoms in the aromatic ring in these compounds differs from that in **IVa** and **VIa**, the chemical shifts of the corresponding carbon atoms ($C^8$ and $C^9$) are significantly different. The $C^8$ signal in the spectra of **IX** and **XI** is shifted downfield relative to **IVa**, **X**, **VIa**, and **VII** owing to the total deshielding effect of *ipso*-Cl, *o*-Br, and *p*-vinyl substituents (134–138 ppm), whereas the $C^9$ signal is shifted upfield (114–118 ppm) owing to the strong shielding effect of the *ipso*-Br and *p*-O atoms. It should be noted also that, owing to the deshielding effect of bromine on the *o*-position, the $C^7$ signal in the spectra of **IVa** and **Va** is shifted downfield relative to phosphorines **IX** and **XI**.



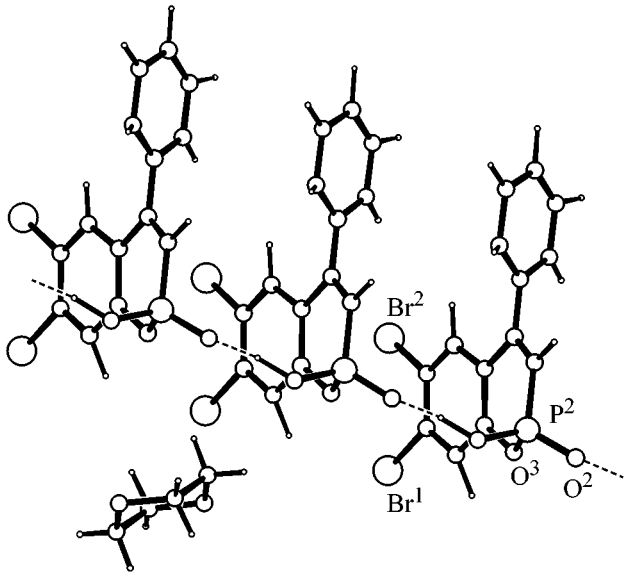
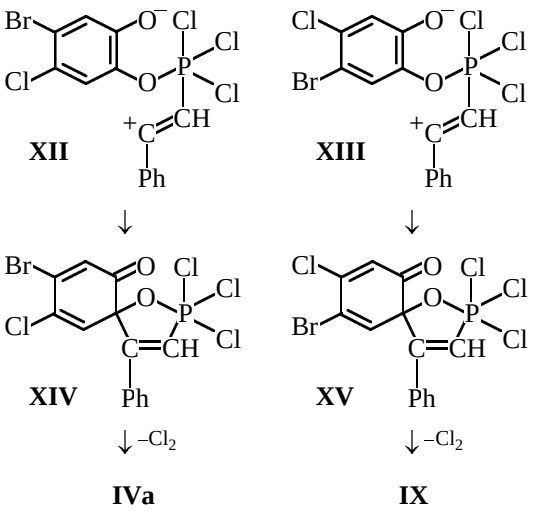




**Fig. 2.** System of hydrogen bonds in the complex of benzophosphorine **Va** with dioxane in the crystal.

Thus, we obtained a very notable result: The bromine atom prefers, to some extent, the *p*-position relative to the oxaphosphorine oxygen atom, and the chlorine atom, the *m*-position. The reaction also yields a noticeable amount of the product of *ipso* subtitution of chlorine for bromine, which is also an indirect evidence of the preferable location of bromine at the *p*-position relative to oxaphosphorine oxygen.

Taking into account the possible reaction schemes suggested in [1, 3], we can tentatively explain the preferableness of *ipso* substitution of oxygen by carbon at the *p*-position relative to the chlorine atom in the benzo fragment of the initial phosphorine. The possible key intermediates of the reaction are phosphorane structures with separated charges of types **XII** and **XIII**, whose formation is followed by the attack of the carbocation at the *ipso*-C atom to give quinoid phospholenes **XIV** and **XV**. These compounds undergo cyclization with release of $Cl_2$ and formation of **IVa** and **IX**. Apparently, intermediate **XIII** is more preferable owing to greater stabilization of the active center with the electron-withdrawing *m*-Cl substituent and to the weaker destabilizing mesomeric effect of the *p*-Br atom. Structure **XII** is less stable because of the weaker electron-withdrawing effect of the *m*-Br atom and stronger destabilizing mesomeric effect of the *p*-Cl atom. This explanation is consistent with the $pK_a$ values of *m*- and *p*-bromine- and -chlorine-substituted phenols [4].




It should be noted also that the product **X** of *ipso* substitution of chlorine for bromine can form only from structure **XV** in which bromine is in the *p*-position relative to oxygen. Therefore, the ratio of products **IVa** and **IX** formed by the competing pathways is actually 3 : 7, i.e., the *p*-bromine-substituted isomer **IX** prevails.

Thus, dihalo-substituted trichlorophosphoranes **II** and **VIII** react with arylacetylenes as readily as does unsubstituted phenylenedioxytrichlorophosphorane **I**, yielding six-membered heterocycles, benzophosphorines. A distinctive feature of the reactions is release of chlorine and partial formation of phosphorines by regioselective *ipso* substitution of chlorine for bromine. When the initial trichlorophosphorane contains two halogen atoms in the benzo fragment, the preferable pathway is *ipso* substitution of oxygen by carbon at the *p*-position relative to chlorine.

## EXPERIMENTAL

The IR spectra were taken on a Specord IR-75 spectrometer (mulls in mineral oil). The NMR spectra were taken on Bruker MSL-400 ($^{13}C$, $^{13}C$–{$^1H$}, 100.6 MHz; $^{31}P$, $^{31}P$–{$^1H$}, 162.0 MHz) and Bruker WM-250 ($^1H$, 250 MHz; $^{31}P$, $^{31}P$–{$^1H$}, 101.6 MHz) spectrometers relative to internal HMDS and external $H_3PO_4$. The $^{13}C$ NMR spectra were taken at 30–35°C.

The mass spectra were measured with an MKh-1310 device interfaced with an SM-4 computer. The ionizing electron energy was 70 eV, and the electron collector current, 30 μA. The samples were introduced through the direct inlet system heated to 120°C. The *m*/*z* values were measured accurately (relative error $5 \times 10^{-5}$) in the automatic mode using reference peaks of perfluorokerosene.

**Single crystal X-ray diffraction study of Va**, 2 : 1 solvate with dioxane, $C_{14}H_9Br_2O_3P \cdot 1/2C_4H_8O_2$. Triclinic crystals, space group *P*1. Unit cell parameters (at 20°C): *a* 4.7932(3), *b* 11.912 (2), *c* 14.930(2) Å; α 81.74(1)°, β 88.11(1)°, γ 82.78(1)°; *V* 836.8(2) Å$^3$; *Z* 2; $d_{calc}$ 1.83 g cm$^{-3}$. The unit cell parameters and the intensities of 3802 reflections, 1146 of which had $I \geq 3\sigma$, were measured on an Enraf-Nonius CAD-4 automated four-circle diffractometer (λMo$K_\alpha$ radiation, graphite monochromator, ω/2θ scanning, $\theta \leq 26.9°$). No decrease in the intensity of the three check reflections was observed during the experiment. The absorption was taken into account empirically (λMo 49.06 cm$^{-1}$): seven reflections with $\chi \geq 80°$ were measured with the ψ-vector rotation with a 10° step. The structure was solved by the direct method using the SIR program [5] and refined first in the isotropic and then in the anisotropic approximation. The hydrogen atoms were revealed from the differential electron density series. Their contribution to structural amplitudes was taken into account with fixed positional and isotropic thermal parameters. The structure was refined to *R* 0.051 and $R_W$ 0.057 (from 1059 unique reflections with $F^2 \geq 3\sigma$). All calculations were performed with an AlphaStation 200 computer using the MolEN program package [6]. The intermolecular interactions were analyzed and the structure drawings obtained using the PLATON program [7]. The atomic coordinates are given in Table 2, and the main geometric parameters, in Table 3. The molecular geometry and the system of hydrogen bonds in the crystal are shown in Figs. 1 and 2.

**5,6-Dibromo-2-chlorobenzo[*d*]-1,3,2-dioxaphosphole 2,2-dichloride (II)**. 4,5-Dibromopyrocatechol (38.1 g) was added in small portions over a period of 1.5–2 h to a stirred solution ot 29.6 g of $PCl_5$ in 150 ml of benzene. After the evolution of HCl ceased, the solvent was distilled off, and the residue was fractionated. Yield of phosphorane **II** 78%, bp 137–141°C (0.1 mm Hg), mp 84–86°C. IR spectrum, ν, cm$^{-1}$: 1130, 1100, 960–980 (POC); 870, 760, 710. $^1H$ NMR spectrum (250 MHz, $CH_2Cl_2$), δ, ppm: 7.25. $^{31}P$ NMR spectrum (162.0 MHz, $CH_2Cl_2$), $\delta_P$, ppm: –24.5. Found, %: Br 39.85; Cl 26.30. $C_6H_2Br_2Cl_3O_2P$. Calculated, %: Br 39.65; Cl 26.39.

**Reaction of phosphorane II with phenylacetylene**. A mixture of 6.8 ml of phenylacetylene and 6 ml of $CH_2Cl_2$ was added dropwise at 10–15°C over a period of 10–15 min to a solution of 13.37 g of **II** in 25 ml of $CH_2Cl_2$, bubbled with argon. The resulting

mixture was allowed to stand for 8 h at 20°C, after which the solvent was distilled off. Vacuum distillation of the residue gave a mixture of isomeric 1,2-dichlorostyrenes, bp 60–65°C (0.1 mm Hg), with the characteristics consistent with the published data [8]. The viscous glassy residue consisting of 88% 6,7-dibromo-4-phenyl-2-chlorobenzo[*e*]-1,2-oxaphosphorin-3-ene 2-oxide (**IIIa**) and 12% 7-bromo-4-phenyl-2,6-dichlorobenzo[*e*]-1,2-oxaphosphorin-3-ene 2-oxide (**IVa**) was examined spectroscopically. Mass spectrum, *m*/*z* ($I_{rel}$, %)[3]: 439 (2.4), 438 (16.5), 437 (11.9), 436 (74.3), 435 (17.7), 434 (100), 433 (10.3), 432 (44.5) [$C_{14}H_8Br_2ClO_2P$] [$M_{\mathbf{IIIa}}$]$^{+\cdot}$; 395 (1.9), 394 (4.1), 393 (4.1), 392 (26.7), 391 (9.5), 390 (52.5), 389 (7.2), 388 (37.1) [$C_{14}H_8BrCl_2O_2P$] [$M_{\mathbf{IVa}}$]$^{+\cdot}$; 404 (0.35), 403 (2.3), 402 (1.3), 401 (9.8), 399 (20.1), 398 (3.8), 397 (12.5) [$M_{\mathbf{IIIa}}$ – Cl]$^+$; 359 (1.5), 358 (0.46), 357 (3.4), 356 (3.4), 355 (14.9), 354 (11.9), 353 (14.6) [$M_{\mathbf{IVa}}$ – Cl]$^+$. **Compound IIIa**. $^1$H NMR spectrum (250 MHz, $CDCl_3$), δ, ppm (*J*, Hz): 7.52 and 7.40 two s ($H^7$, $H^{10}$); 7.43 and 7.28 two m ($C_6H_5$); 6.30 d (PCH, $^2J_{PCH}$ 23.8). $^{31}$P NMR spectrum (162.0 MHz, $CDCl_3$), $\delta_P$, ppm (*J*, Hz): 17.3 d ($^2J_{PCH}$ 24.0).

A mixture of **IIIa** and **IVa** (7.2 g) was dissolved in 20 ml of dioxane and treated with 0.3 ml of $H_2O$. A white clotted precipitate formed, consisting of 90–92% 6,7-dibromo-2-hydroxy-4-phenylbenzo[*e*]-1,2-oxaphosphorin-3-ene 2-oxide (**Va**) and 8–10% 7-bromo-2-hydroxy-4-phenyl-6-chlorobenzo[*e*]-1,2-oxaphosphorin-3-ene 2-oxide (**VIa**), which was filtered off and washed with diethyl ether. Recrystallization from dioxane and ethanol yielded phosphonic acid **Va** as a dioxane complex; yield 47%, mp 220–222°C. IR spectrum, ν, cm$^{-1}$: 2500–2600, 2250 (POH); 1580, 1536, 1260–1270, 1215, 1187, 1120, 1005, 975, 900, 870, 805, 760, 720, 705. $^1$H NMR spectrum (250 MHz, DMF-$d_7$), δ, ppm (*J*, Hz): 7.70 s (1H, $H^{10}$); 7.50 and 7.46 two m (5H, $C_6H_5$); 7.36 s (1H, $H^7$); 6.38 d (1H, PCH, $^2J_{PCH}$ 17.0); 3.53 s (4H, dioxane); 11.30 br. s (1H, OH). $^{31}$P NMR spectrum (162.0 MHz, DMF-$d_7$), $\delta_P$, ppm (*J*, Hz): 3.0 d ($^2J_{PCH}$ 17.0). Found, %: C 41.51; H 2.78; Br 35.07; P 7.01. $C_{14}H_9Br_2O_3P \cdot 1/2C_4H_8O_2$. Calculated, %: C 41.73; H 2.82; Br 34.78; P 6.73.

By a similar procedure, starting from 6.01 g of **II** and 4.05 g of *p*-chlorophenylacetylene, we obtained a mixture of 92% 6,7-dibromo-2-chloro-4-(*p*-chlorophenyl)benzo[*e*]-1,2-oxaphosphorin-3-ene 2-oxide (**IIIb**) and 8% 7-bromo-4-phenyl-2,6-dichlorobenzo-[*e*]-1,2-oxaphosphorin-3-ene 2-oxide (**IVb**). **Compound IIIb**. $^1$H NMR spectrum (60 MHz, $CCl_4$), δ, ppm (*J*, Hz): 6.27 d (PCH, $^2J_{PCH}$ 23.0). $^{31}$P NMR spectrum (162.0 MHz, $CH_2Cl_2$), $\delta_P$, ppm (*J*, Hz): 16.2 d ($^2J_{PCH}$ 23.0). **Compound IVb**. $^{31}$P NMR spectrum (162.0 MHz, $CH_2Cl_2$), $\delta_P$, ppm (*J*, Hz): 15.1 d ($^2J_{PCH}$ 23.0).

Hydrolysis of the mixture of **IIIb** and **IVb** in dioxane gave a mixture of 90–92% 6,7-dibromo-2-hydroxy-4-(*p*-chlorophenyl)benzo[*e*]-1,2-oxaphosphorin-3-ene 2-oxide (**Vb**) and 8–10% 7-bromo-2-hydroxy-4-(*p*-chlorophenyl)-6-chlorobenzo[*e*]-1,2-oxaphosphorin-3-ene 2-oxide (**VIb**). Phosphorine **Vb** was isolated in a 37% yield by crystallization from dioxane; mp 312–315°C. IR spectrum, ν, cm$^{-1}$: 2540–2580, 2250–2300 (POH); 1600, 1590, 1535 (C=C, C=$C_{arom}$); 1490, 1375, 1330 [δ(CH)]; 1250, 1200–1211, 1133, 1115, 1098, 1020–1030, 970, 920, 892, 859, 847, 812, 720, 585, 555, 530, 500. $^1$H NMR spectrum (400 MHz, ethanol-$d_6$ + 30% DMSO), δ, ppm (*J*, Hz): 7.51 and 7.20 two s (2H, $H^7$ and $H^{10}$); 7.43 and 7.29 two m (4H, Cl–$C_6H_4$, *AA'XX'* pattern, $^3J_{AX} = {}^3J_{A'X'}$ = 8.5); 6.23 d (1H, PCH, $^2J_{PCH}$ 17.2). $^{31}$P NMR spectrum (162.0 MHz, DMSO), $\delta_P$, ppm: 3.52. Found, %: C 37.24; H 1.83; P 6.42. $C_{14}H_8Br_2ClO_3P$. Calculated, %: C 37.29; H 1.78; P 5.42. From the mother liqour, after separation of **Vb** and evaporation followed by crystallization, we obtained a mixture of **Vb** and **VIb** in a 3 : 1 ratio. Compound **VIb**. $^1$H NMR spectrum (400 MHz, ethanol-$d_6$ + 30% DMSO), δ, ppm (*J*, Hz): 7.52 and 7.06 two s (2H, $H^7$ and $H^{10}$); 7.43 and 7.29 two m (4H, Cl–$C_6H_4$, *AA'XX'* pattern, $^3J_{AX} = {}^3J_{A'X'}$ = 8.5); 6.24 d (1H, PCH, $^2J_{PCH}$ 17.0). $^{31}$P NMR spectrum (162.0 MHz, DMSO), $\delta_P$, ppm: 3.6.

**5-Bromo-2,6-dichlorobenzo[*d*]-1,3,2-dioxaphosphole 2,2-dichloride (VIII)**. A solution of 15.03 g of 4-bromo-5-chloropyrocatechol in 100 ml of benzene was added dropwise with stirring to a solution of 21.9 g of $PCl_5$ in 200 ml of benzene. After the evolution of HCl ceased, the solvent was distilled off, and the residue was fractionated. Yield of phosphorane **VIII** 69%, bp 156–158°C (0.2 mm Hg). $^{13}$C NMR spectrum (100.6 MHz, $CDCl_3$), $\delta_C$, ppm (in parentheses are the $\delta_C$ values, ppm, calculated according to [9] with the use of base chemical shifts of 2-chlorobenzo[*d*]-1,3,2-dioxaphosphole 2,2-dichloride instead of benzene) (*J*, Hz): 141.28 (143.2) s (br. d.d) ($C^5$, $J_{HC^7CC^5}$ 8.0, $J_{HC^{10}C^5}$ 4.4); 141.94 (143.3) d (d.d.d) ($C^6$, $J_{HC^{10}CC^6}$ 8.0, $J_{HC^7C^6}$ 4.5, $J_{POC^6}$ 1.1); 112.45 (113.3) d (d.d.d) ($C^7$, $J_{POC^6C^7}$ 17.6, $J_{HC^7}$ 173.0, $J_{HC^{10}CCC^7}$ 1.2); 128.69 (129.8) s (d.d) ($C^8$, $J_{HC^{10}CC^8}$ 8.6, $J_{HC^7C^8}$ 4.5); 115.49 (114.9) s (d.d) ($C^9$, $J_{HC^7CC^9}$ 8.0, $J_{HC^{10}C^9}$ 4.2); 115.54 (116.1) d (d.d.d) ($C^{10}$, $J_{POC^5C^{10}}$ 17.4, $J_{HC^{10}}$ 173.6, $J_{HC^7CCC^{10}}$ 0.9). $^{31}$P NMR

[3] The ions containing the most abundant isotopes are given.

spectrum (162.0 MHz, $CH_2Cl_2$), $\delta_P$, ppm: –24.3. Found, %: Cl 39.87. $C_6H_2BrCl_4O_2P$. Calculated, %: Cl 39.55.

**Reaction of phosphorane VIII with phenylacetylene**. A solution of 2.6 ml of phenylacetylene in 40 ml of $CH_2Cl_2$ was added dropwise at 10–15°C over a period of 10–15 min to a solution of 8.8 g of **VIII** in 80 ml of $CH_2Cl_2$, bubbled with argon. The mixture was allowed to stand at 20°C for 8 h, after which the solvent was distilled off. Vacuum distillation of the residue gave a mixture of isomeric 1,2-dichlorostyrenes. The glassy residue was a mixture of 31% 7-bromo-4-phenyl-2,6-dichlorobenzo[*e*]-1,2-oxaphosphorin-3-ene 2-oxide (**IVa**), 51% 6-bromo-4-phenyl-2,7-dichlorobenzo[*e*]-1,2-oxaphosphorin-3-ene 2-oxide (**IX**), and 18% 4-phenyl-2,6,7-trichlorobenzo[*e*]-1,2-oxaphosphorin-3-ene 2-oxide (**X**). The products were identified spectroscopically. **Compound IX**. $^1$H NMR spectrum (250 MHz, $CDCl_3$), δ, ppm (*J*, Hz): 6.38 d (PCH, $^2J_{PCH}$ 23.8). $^{31}$P NMR spectrum ($CDCl_3$), $\delta_P$, ppm: 15.4.

The mixture of **IVa**, **IX**, and **X** was dissolved in 100 ml of dioxane and treated with 0.3 ml of water. Within 5–10 h, an abundant white precipitate formed, consisting of phosphorines **VI**, **VII**, and **XI**; it was recrystallized from ethanol, methanol, and dioxane. Mixtures of **VI**, **VII**, and **XI** (complexes with dioxane) in various ratios were obtained. **Compound XI**. $^1$H NMR spectrum (250 MHz, ethanol-$d_6$), δ, ppm (*J*, Hz): 6.10 d (PCH, $^2J_{PCH}$ 17.6). $^{31}$P NMR spectrum (ethanol-$d_6$), $\delta_P$, ppm (*J*, Hz): 4.36 d ($^2J_{PCH}$ 17.6). Compounds **VIa** and **VII** were obtained by independent synthesis according to [1]. Mass spectrum of the complex of **VIa** with dioxane, *m*/*z* ($I_{rel}$, %): 375 (1.8), 374 (12.0), 373 (8.2), 372 (50.4), 371 (9.3), 370 (38.7) $[M_{\mathbf{VIa}}]^{+\cdot}$, 369 (3.0) $[M_{\mathbf{VIa}} - H]^+$, 353 (3.0) $[M_{\mathbf{VIa}} - OH]^+$, 335 (2.1) $[M_{\mathbf{VIa}} - Cl]^+$, 256 (23.7) $[M_{\mathbf{VIa}} - Cl - Br]^+$, 199 (36.8), 163 (100.0) $[C_{13}H_7]^+$, 88 (90.4) $[C_4H_8O_2]^+$.

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