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The structure of products of reaction of *o*-phenylenedioxytrichlorophosphorane with arylacetylenes

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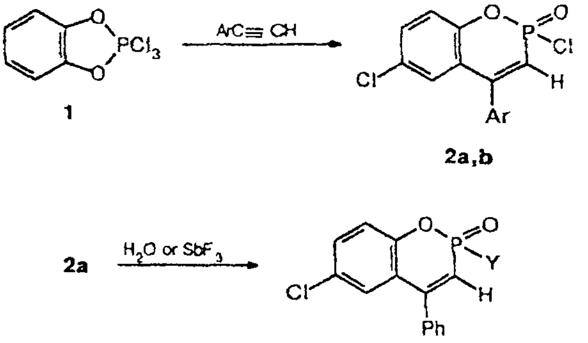
The products of reaction of *o*-phenylenedioxytrichlorophosphorane with arylacetylenes were identified as 4-aryl-2-chloro-2-oxo-5,6-(4-chlorobenzo)phosphorin-3-enes using ^{1}H, ^{13}C, ^{31}P NMR, and IR spectroscopy and high-resolution mass spectrometry.

Key words: *o*-phenylenedioxytrichlorophosphorane, arylacetylenes, chlorination, *ipso*-substitution, 2-chloro-2-oxo-4-phenyl-5,6-(4-chlorobenzo)phosphorin-3-enes.

Reaction of phenylacetylene with PCl_5 has been studied in detail.[1] Depending on the ratio of the starting compounds and temperature, phosphonium salts, phosphoranes, or derivatives of P^{III} are formed.[1—5] Reactions of phenylacetylene with phosphoranes $PhCH=CHPCl_4$ and $PhPCl_4$ are also described,[3,6] but the structures of the adducts that are formed initially, have not been studied. Some published data indicate[7,8] that the structures of the adducts strongly depend on the substituent type in acetylene.

We studied the reaction of phenylacetylene with *o*-phenylenedioxytrichlorophosphorane **1** containing a benzodioxaphospholane fragment, which effectively stabilizes the pentacoordinated state of phosphorus.[9] Unlike PCl_5, chlorophosphorane **1** has the phosphorane structure in both polar and non-polar solvents.[9] Compound **1** adds easily, with exothermic effect, to phenyl- and *para*-bromophenylacetylenes to give products **2a,b**. The structure of compound **2a** differs from that proposed earlier[10] for the product of interaction of chlorophosphorane **1** with PCl_5.

Table 1 summarizes ^{13}C NMR spectral data of compounds **2** isolated in the crystalline state and of acid **3**, the product of hydrolysis of compound **2a**. The presence of a doublet of doublets at δ 115.6 with large spin-spin coupling constants ($^1J_{PC}$ = 154 and 165—172 Hz) suggests the formation of a P—CH=C fragment. Five signals of the carbon atoms, which are not connected with the protons, are observed in the spectrum of compound **2a**. Three low-field signals at δ 155.82, 149.77, and 136.8 correspond to the carbon atoms C(7), C(1), and C(9). According to its chemical shift, the last signal (doublet, $^3J_{C(9)P}$ = 20.94 Hz) is similar to that of the *ipso*-carbon atom of the aromatic ring in styrene derivatives.[11] The cyclic structure of compound **2a** is also confirmed by the multiplicity of the signal of C(6) ($^3J_{C(6)P}$ = 15.7—18.2 Hz, $^3J_{C(6)H(8)}$ = 6.0—7.5 Hz, $^3J_{C(6)H(2)}$ = 7.5 Hz). An estimate of the $^3J_{C(6)P}$ value performed on the basis of published data[12] gives a value of 16 Hz for two bond channels (PCCC(6) and POCC(6)). The value of $^3J_{POCC(2)}$ ~ $^3J_{PC=CCcis}$ = ~8 Hz) was used as a model. Taking into account the results published earlier[13] as well as the pattern of spin-spin coupling constants in the ^{1}H and ^{13}C NMR spectra, the signal at δ 130.41 was assigned to the carbon atom C(4) linked with the chlorine atom. Spin-spin coupling constants J_{CH} of the carbon atoms of the benzene ring were interpreted with account of the known data ($^2J_{CCH}$ = 0—4 Hz and $^3J_{CCCH}$ = 6—11 Hz).[14]



1

2a,b

3 or **4**

2: Ar = Ph (**a**), 4-BrC$_6$H$_4$ (**b**)
3: Y = OH
4: Y = F

The presence of the P—CH=C fragment is also confirmed by the data from the ^{1}H NMR spectra of

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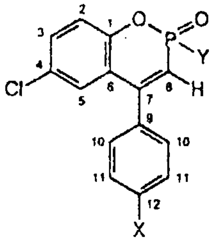
Table 1. The parameters of the ^{13}C NMR spectra of compounds **2a**, **2b**, and **3**



X, Y = H, Cl (**2a**); Br, Cl (**2b**); H, OH (**3**)

Atom	**2a**		**2b**		**3**	
	$\delta^{13}C$	J/Hz	$\delta^{13}C$	J/Hz	$\delta^{13}C$	J/Hz
C(1)	149.77 (dddd)	10.2 (POC(1)) 9.9 (CCC(3)H) 9.9 (CCC(5)H) 4.5 (CC(2)H)	149.40 (br.m)	10.0 (POC) ~8.0—9.0 (CCC(3)H) ~8.0—9.0 (CCC(5)H) 3.6 (CC(2)H)	150.12 (dddd)	6.9 (POCC) 9.3 (CCC(3)H) 9.0—10.0 (CCC(5)H) ~4.0 (CC(5)H)
C(2)	121.37 (dd)	168.6 (CH) 7.8 (POCC)	121.23 (dd)	162.0 (CH) 8.0 (POCC)	120.79 (dd)	167.5 (CH) 7.0 (POCC)
C(3)	132.36 (dd)	169.9 (CH) 6.2 (CCC(2)H)	128.95 (ddd)	162 (CH) ~4.5 (CCH) 1.5 (POCCC)	130.11 (dd)	164.0 (CH) 6.2 (CCCH)
C(4)	130.41 (br.dm)	11.7 (CCC(2)H) ~2—3 (CC(3)H) 1.2 (POCCCC)	130.44 (br.m)	1.5 (POCCCC)	126.90 (br.dt)	11.6 (CCC(2)H) 3.2 (CC(3)H) 3.3 (CC(5)H)
C(5)	129.48 (dd)	168.9 (CH) 5.4 (CCC(3)H)	132.64 (dm)	159.0—162.0 (CH)	127.37 (dd)	165.2 (CH) 5.7 (CCCH)
C(6)	123.07 (br.ddd)	18.2 (PCCC) ~7.4 (CCC(2)H) ~6.2 (CCC(8)H)	122.31 (d)	17.6 (PCCC) 7.5 (CCC(2)H) 7.5 (CCC(8)H)	123.54 (dd)	~15.7 (PCCC) ~7.5 (CCC(2)H) ~6—7 (CCC(8)H)
C(7)	155.82 (br.s)	1.3 (PCC)	154.30 (br.m)	2.0 (PCC)	150.52 (br.s)	—
C(8)	115.68 (dd)	154 (PC) 171.7 (CH)	115.67 (dd)	154.2 (PC) 165.7 (CH)	117.12 (dd)	169.2 (PC) 163.3 (CH)
C(9)	136.80 (br.dt)	20.9 (PCCC) ~6.5 (CCC(11)H)	135.33 (dddt)	21.0 (PCCC) ~7.0—8.0 (CCC(8)H) ~6 (CCC(11)H) ~1—2 (CC(10)H)	137.92 (br.dt)	20.4 (PCCC) ~7.2 (CCC(11)H)
C(10)	128.58 (dm)	162.1 (CH) 6.5 (CCC(10′)H) 5.4 (CCC(12)H) ~3.5 (CC(11)H)	129.89 (dd)	155.4 (CH) 6.5 (CC(10′)H)	128.03 (br.m)	160.7 (CH) 6.5 (CCC(10′)H) ~6.5 (CCC(12)H) ~3.5 (CC(11)H)
C(11)	129.22 (br.dd)	162.4 (CH) 6.7 (CCC(11′)H)	132.30 (br.d)	159.0—162.0 (CH)	128.38 (br.d)	161.5 (CH) 6.4 (CCC(11′)H)
C(12)	130.29 (br.dt)	162.0 (CH) 7.5 (CCC(10)H)	124.60 (tt)	9.5 (CCC(10)H) 3.0 (CC(11)H)	128.62 (br.dt)	161.4 (CH) 7.5 (CCC(10)H) 7.5 (CCC(10′)H)

phosphorine **2a**: the doublet at δ 6.31 ($^2J_{PCH}$ = 24 Hz) transforms into a singlet upon $^1H-\{^{31}P\}$ selective spin decoupling. The chemical shift, δP 18, of the product **2a** unambiguously attests to the presence of P^{IV}. Thus, a phosphoryl group forms, *ipso*-substitution of the aromatic oxygen occurs, and the benzene ring is chlorinated in the reaction under discussion. The structure of **2** is also supported by the results of hydrolysis and fluorination of the product **2a**. The latter reaction gives fluorophosphorine **4**, whose ^{31}P NMR spectrum has a characteristic doublet (δP 9, $^1J_{PF}$ = 1064 Hz).

The structures of compounds **2a,b** were confirmed by the data from high-resolution mass spectrometry: intense peaks with *m/z* 310 and 388 correspond to molecular ions, and the main fragmentation processes correspond to formation of $[M-Cl]^+$ and $[M-Cl-PO]^+$ ions. The composition of the ions was confirmed by high-resolution spectra.

Experimental

The ^1H and $^1H-\{^{31}P\}$ NMR spectra were recorded on a Varian HA 100D instrument (100 MHz) in CD_2Cl_2, and ^1H NMR spectrum of compound **2b** was recorded on a Varian Unity 300 instrument (300 MHz) in $CDCl_3$. The ^{13}C and $^{13}C-\{^1H\}$ NMR spectra were obtained on a Bruker MSL-400 instrument (100.6 MHz) in DMF-d_7 (compound **3**) and $CDCl_3$ (the others). The IR spectra were recorded on a Specord M-80 instrument for suspensions in vaseline oil. The mass spectra were measured on an MKh-1310 instrument combined with an SM-4 computer. Electron ionization energy was 70 eV, and collector current was 30 μA. The substance was injected directly into the ion source at 100 °C. The exact values of molecular masses were determined automatically from reference peaks of perfluorokerosene with an accuracy of no less than 5×10^{-6} amu.

Reaction of *o*-phenylenedioxytrichlorophosphorane 1 with phenylacetylene. Phenylacetylene (40 mmol) in 10 mL of CH_2Cl_2 was added dropwise with intense stirring in an argon atmosphere to a solution of phosphorane **1** (20 mmol) in 50 mL of CH_2Cl_2 (−10 °C). The mixture was kept at 20 °C for 3 h, and the solvent was concentrated to half *in vacuo*. The residue crystallized after 1—2 days, and the crystals were washed with a cold mixture CH_2Cl_2—*n*-C_5H_{12} (5 : 1) and dried *in vacuo*. 2-Chloro-2-oxo-4-phenyl-5,6-(4-chlorobenzo)phosphorin-3-ene (**2a**) was obtained, yield 87%, m.p. 122—124 °C. IR, ν/cm^{-1}: 3000 (CH arom.); 1576, 1556, 1525 (C=C, C=C arom.); 1477, 1427, 1383, 1367, 1322 (δ(CH)); 1282 (P=O); 1264, 1250, 1211, 1194, 1168, 1134, 1093, 1073, 1060, 1014, 944, 914, 894, 876, 809 (POC, CCl); 792, 747, 733, 715, 683, 656, 600, 552, 521, 512 (PCl). MS, *m/z* (I_{rel}(%)): 314 (12), 313 (9.0), 312 (62), 311 (17), 310 $M^{+\cdot}$ $[C_{14}H_9Cl_2O_2P]^{+\cdot}$* (100), 285 (0.60), 283 (4.0), 281 $[M-CHO]^+$ (5.5), 278 (2.2), 277 (13), 276 (7.8), 275 $[M-Cl]^+$ (40), 240 (2.4), 239 $[M-Cl-HCl]^+$ (16), 230 (7.7), 229 (4.1), 228 $[M-Cl-PO]^+$ (24), 164 (9.1), 163 $[C_{13}H_7]^+$ (12), 106 (0.90), 105 $[C_7H_5O]^+$ (10).

Reaction of phosphorane 1 with 4-bromophenylacetylene. 4-(4-Bromophenyl)-2-chloro-2-oxo-5,6-(4-chlorobenzo)phosphorin-3-ene **2b** was obtained according to a similar procedure, yield 92%, m.p. 143—145 °C, δP 19. (CH_2Cl_2). ^1H NMR, δ: 6.32 (d, 1 H, PCH, $^2J_{PCH}$ = 23.3 Hz); 7.11 (d, 1 H, H(5), $^4J_{H(5)CCCH(3)}$ = 2.5 Hz); 7.19 (d, 2 H, H(10), $^3J_{H(11)CCH(10)}$ = 8.6 Hz); 7.22 (d, 1 H, H(2), $^3J_{H(2)CCH(3)}$ = 8.8 Hz); 7.39 (ddd, 1 H, H(3), $^3J_{H(2)CCH(3)}$ = 8.8 Hz, $^4J_{H(5)CCCH(3)}$ = 2.5 Hz, $^5J_{POCCCH(3)}$ = 1.6 Hz); 7.58 (d, 2 H, H(11), $^3J_{H(11)CCH(10)}$ = 8.6 Hz). IR, ν/cm^{-1}: 1584, 1568, 1540 (C=C); 1504, 1424, 1400, 1392, 1350, 1316 (δ(CH)); 1296, 1220, 1152, 1124, 1112, 1048, 1008, 976, 928 (POC, P=O); 900, 856, 812, 730, 710. MS, *m/z* (I_{rel} (%)): 394 (7.7), 393 (7.4), 392 (49), 391 (18), 390 (100), 389 (11), 388 $M^{+\cdot}$ $[C_{14}H_8BrCl_2O_2P]^{+\cdot}$ (63), 361 (6.0), 359 $[M-CHO]^+$ (3.8), 357 (5.2), 355 (21), 353 $[M-Cl]^+$ (18), 319 (2.8), 317 $[M-Cl-HCl]^+$ (2.7), 310 (4.2), 309 (3.4), 308 $[M-HBr]^+$ (14), 307 (1.9), 366 $[M-Cl-PO]^+$ (9.8), 245 $[C_{13}H_7ClOP]^+$ (1.6), 199 $[C_{13}H_8Cl]^+$ (5.1), 164 (10), 163 $[C_{13}H_7]^+$ (18), 105 $[C_7H_5O]^+$ (0.41).

Hydrolysis of phosphorine 2a. Water (0.18 mL) was added dropwise at 20 °C to a solution of phosphorine **2a** (10 mmol) in 50 mL of dioxane. The reaction is exothermic and formation of a white precipitate was observed. The precipitate was filtered off, washed with ether, and dried. 2-Hydroxy-2-oxo-4-phenyl-5,6-(4-chlorobenzo)phosphorine-3-ene (**3**) was obtained, yield 89%, m.p. 228 °C. IR, ν/cm^{-1}: 2500 (OH); 1530, 1550 (C=C); 1367, 1340 (δ(CH)); 1240 sh, 1190—1220 (P=O, POC); 1115, 1005, 967 (POC); 820 (CCl); 792, 747, 733, 715, 683, 656, 600, 552, 521, 512 (PCl). Found (%): C, 57.51; H, 3.88; Cl, 12.0; P, 11.07. $C_{14}H_{10}ClO_3P$. Calculated (%): C, 57.46; H, 3.44; Cl, 12.11; P, 10.58.

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* The peaks of ions containing the most abundant isotopes are indicated.