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The Reaction of Triphenylmethylhalophosphines with Tetrachloro-orthobenzoquinone: Oxidation—Isomerization—Dehydrohalogenation

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ABSTRACT: *Treatment of solutions of the halophosphines TrtP(H)F (Trt = trityl, Ph_3C)* **1a** *and TrtP(H)Cl* **1b** *with equimolar amounts of TOB (tetrachloro-orthobenzoquinone) led to the formation of mixtures of products. They contained the phosphoranes* **2a** *and* **2b***, which were formed by oxidation with TOB and are in equilibrium with the phosphines* **3a** *and* **3b***. Moreover, the trityl phosphonite* **4***, which was formed by dehydrohalogenation of* **2a***,* **2b** *and* **3a***,* **3b***, was observed in both mixtures. The dehydrohalogenation was found to be reversible in the case of HF. The pure compounds* **4** *and* **5** *were obtained from the reaction of $TrtPCl_2$ with tetrachlorocatechol* **4** *and by the oxidation of* **1a** *and* **1b** *with two equivalents of TOB. Because of its importance in this reaction sequence, an X-ray crystal structure determination was carried out on* **4***. The P–O bond lengths of 168.4(2) and 167.7(2) pm are probably to be attributed to a bond-lengthening effect of the chlorine atoms of the quinone. As a comparison with analogous systems reveals, the phosphorane* **5** *is an example of a $\sigma^5\lambda^5$(P) species in which the phosphorus atom exhibits square-pyramidal coordination.* © 1999 John Wiley & Sons, Inc. Heteroatom Chem 10: 277–280, 1999

INTRODUCTION

Halophosphines of the type RP(H)X (X = F, Cl, Br), formally halides of the unknown hypophosphonous acids RP(H)OH [1], belong to the least investigated class of organophosphorus compounds [2,3]. They should reveal the reaction behavior attributed both to the P-H and to the P-X function. Furthermore, they may be considered as hydrogen halide adducts of the corresponding phosphinidenes RP. A suitable reagent to "trap" these species is the strong oxidant tetrachloro-orthobenzoquinone (TOB), which is widely used in organophosphorus chemistry to obtain phosphoranes from σ^3(P) compounds [4]. Depending on the substitution pattern at the phosphorus atom, rearrangement/isomerization of these phosphoranes can occur subsequent to the oxidation with TOB [5,6].

RESULTS AND DISCUSSION

When solutions of the triphenylmethyl-substituted halophosphines TrtP(H)X **1a** and **1b** (**1a**: X = F, **1b**: X = Cl) were treated with equimolar amounts of TOB, mixtures of compounds were formed within 10

Dedicated to Professor Wilhelm Preetz on the occasion of his 65th birthday.

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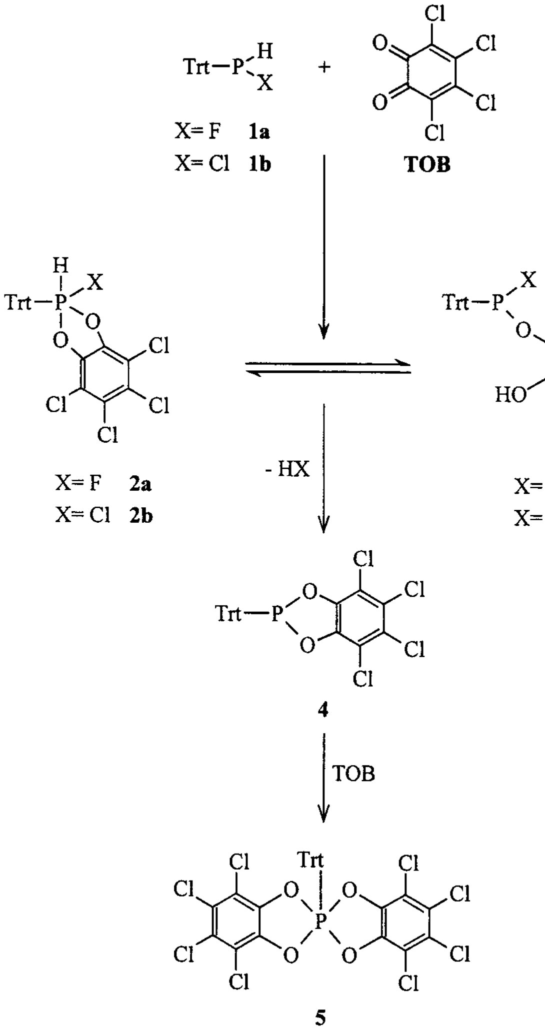
minutes in a smooth reaction. Based on ^{31}P NMR spectroscopic data, and on the independent synthesis of several compounds, a course of reaction as depicted in Scheme 1 is suggested:

Oxidation of the phosphorus atom in **1a** and **1b** furnished the hydrophosphoranes **2a** and **2b** in the initial step. The δ(P) values of both species were observed in a region typical of phosphoranes (**2a**: -12.7 ppm, **2b**: -16.7 ppm) [7]. Also, the magnitude of ^1J(PH) (**2a** and **2b**) and ^1J(PF) (**2a**) is characteristic of phosphoranes and proves the anticipated structures [7]. Through ring-opening and proton migration from phosphorus to oxygen in **2a** and **2b**, probably in an equilibrium, the σ^3(P) species **3a** and **3b** are formed. Distinction of **3a** and **3b** from **2a** and **2b** is easy, because of the greatly differing ^{31}P NMR parameters. As expected for σ^3(P) species, δ(P) is shifted considerably to lower field (**3a**: 208.5 ppm, **3b**: 183.8 ppm); no phosphorus-proton coupling was observed. The magnitude of ^1J(PF) found for **3a** (1179.4 Hz) is characteristic of fluorophosphites/-phosphines [7]. It was not surprising that by elimination of HF or HCl, the cyclic phosphonite **4** was formed in the next step [8]. However, significant differences exist between HF and HCl adducts (vide infra). It still remains unclear whether the elimination of HF/HCl started from **2a** and **2b** or from **3a** and **3b**. Because the reaction of **4** with TOB was obviously faster than that of **1b** or **3b**, **4** was partially oxidized, yielding the phosphorane **5** as the final product. As a consequence, in the case of X = F, a mixture of **1a**, **2a**, **3a**, and **4**, and in the case of X = Cl, a mixture of **1b**, **2b**, **3b**, **4**, and **5** was observed.



SCHEME 1

In order to confirm the anticipated reaction course, the following investigations were carried out:

a. The phosphonite **4** was independently synthesized from $TrtPCl_2$ and tetrachlorocatechol in the presence of triethylamine.
b. Whereas treatment of **4** with HF (as $NEt_3 \cdot 3\,HF$) readily yielded a mixture of **2a**, **3a**, and **4**, no reaction was observed when **4** was treated with excess HCl in ether, even over extended periods of time. This may be due to the increased strength of the P–F bond, compared to the P–Cl bond, which makes the adduct formation thermodynamically more favorable in the case of HF than of HCl.
c. Treatment of **1a** and **2a** with two equivalents of TOB selectively furnished the phosphorane **5** in good yields.

As a key compound in the reaction sequence, the phosphonite **4** was also studied by X-ray crystallography. Its structure in the solid state is depicted in Figure 1.

DISCUSSION OF THE STRUCTURE OF 4

The structure of compound **4** can be compared to that of bis(benzo-1,3,2-dioxaphospholanyl)-dichloromethane **Y** [9], which represents the only known structure of a carbon-substituted 1,3,2σ^3-dioxaphospholane.

The heterocycle of compound **4** is, like one of those in **Y**, nearly planar with a mean deviation of 2.3 pm. The phosphorus atom displays the expected pyramidal conformation in which the phosphorus atom lies 84.3 pm outside the plane of its α substituents. The endocyclic angle O1–P–O2 is the smallest angle at phosphorus.

The P–O bonds of **4** are significantly longer than those of **Y** [165.5(2) pm to 166.5(2) pm]. The tendencies of the P–O bond lengths of catechol groups are clear from the phosphorate **Z** [with $(Me_2NCHO)_2H^+$ as counterion] [10], in which the P–O bond lengths

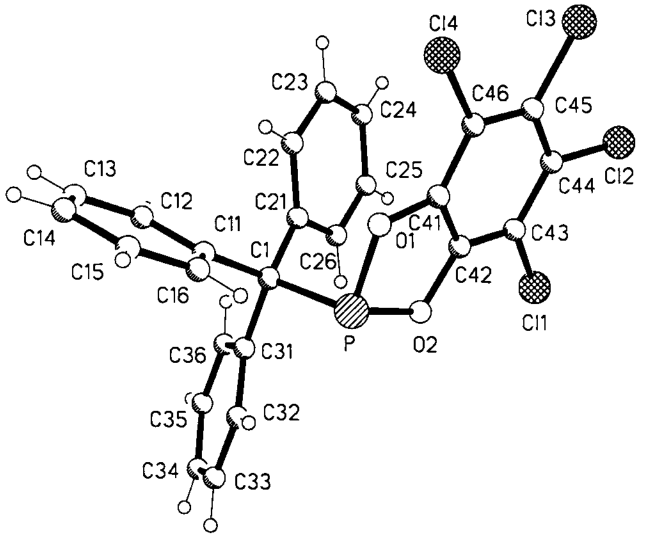


FIGURE 1 The molecule of **4** in the crystal. Radii are arbitrary. Selected bond lengths [pm] and angles [°]: P-O(2) 167.70(15), P-O(1) 168.41(15), P-C(1) 191.35(21), O(1)-C(41) 137.11(23), O(2)-C(42) 137.47(24), C(1)-C(21) 153.02(27), C(1)-C(11) 153.79(28), C(1)-C(31) 154.21(28), O(2)-P-O(1) 93.65(7), O(2)-P-C(1) 102.36(8), O(1)-P-C(1) 100.32(8), C(41)-O(1)-P 110.14(12), C(42)-O(2)-P 110.27(12), C(21)-C(1)-C(11) 114.00(17), C(21)-C(1)-C(31) 115.56(17), C(11)-C(1)-C(31) 106.62(16), C(21)-C(1)-P 106.79(13), C(11)-C(1)-P 107.79(13), C(31)-C(1)-P 105.53(14).

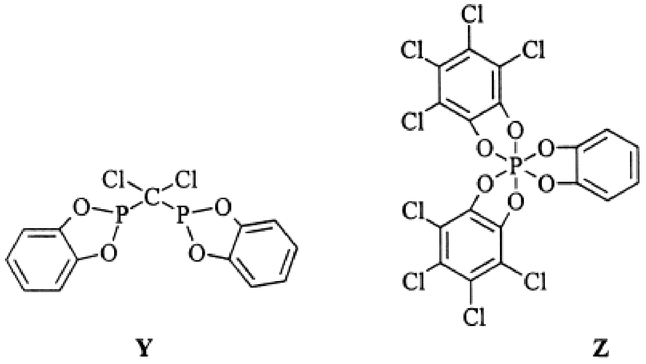


FIGURE 2

to the tetrachlorocatechol groups are 172.1(3) and 172.9(3) pm, that is, much longer than the P–O lengths to the unsubstituted catechol of **Z**, 168.8(3) pm (see Figure 2) (because of crystallographic twofold symmetry, only three independent bond lengths are observed). This means that the influence of the triphenylmethyl group on the geometry at the phosphorus atom in **4** is marginal.

The bicyclic phosphorane **5** is of interest for another reason: Holmes et al. found for analogous (R = Ph) and similar bicyclic systems that these species, depending on the groups bonded to phosphorus, show a tendency to exist in a more or less ideal square-pyramidal structure in the solid state [7,8,11]. In contrast, the majority of phosphoranes favor a trigonal-bipyramidal coordination at phosphorus. Although no unequivocal decision is possible, the δ(P) value of **5** (2.4 ppm) and the fact that the triphenylmethyl group is sterically more demanding than the phenyl group suggest the same coordination at phosphorus in **5** [12].

EXPERIMENTAL

Working conditions were as described elsewhere [13]. Proton decoupling of heteroatom NMR spectra was used, except when indicated otherwise. The following compounds were synthesized according to literature procedures: TrtP(H)F [14], TrtP(H)Cl [14], and TrtPCl$_2$ [15].

Reaction of Triphenylmethylfluorophosphine **1a** *with TOB (1 Eq.).* At room temperature, a solution of 0.03 g (0.1 mmol) of triphenylmethylfluorophosphine **1a** and 0.025 g (0.1 mmol) of TOB in 0.5 mL of deuterochloroform were placed in a 5 mm NMR tube. After 10 minutes, the reaction mixture was investigated by ^{31}P NMR spectroscopy. ^{31}P NMR (CDCl$_3$, ^{1}H coupled): $\delta = -12.7$ [dd, ^{1}J(PF) = 880.8 Hz, ^{1}J(PH) = 818.2 Hz, 15%, **2a**], 192.0 [d, ^{1}J(PF) = 1179.4 Hz, 80%, **3a**], 208.5 [s, 5%, **4**].

Reaction of Triphenylmethylchlorophosphine **1b** *with TOB (with 1 Eq.).* At r.t., a solution of 0.04 g (0.1 mmol) of triphenylmethylchlorophosphine **1b** and 0.032 g (0.13 mmol) of TOB in 0.5 mL of deuterochloroform was placed in a 5 mm NMR tube. A ^{31}P NMR investigation after 10 minutes revealed the following compounds: $\delta = -16.7$ [d, ^{1}J(PH) = 943.7 Hz, 15%, **2b**], 2.4 [s, 30%, **5**], 45.5 [d, ^{1}J(PH) = 190.4 Hz, 30%, **1b**], 183.8 [s, 10%, **3b**], 208.5 [s, 15%, **4**].

*2-Triphenylmethyl-3,4,5,6-tetrachlorobenzo-1,3,2-dioxaphospholane (***4***).* To a solution of 2.0 g (5.8 mmol) of triphenylmethyldichlorophosphine and 1.44 g (5.80 mmol) of tetrachlorocatechol in 20 mL of dichloromethane was added at r.t. 1.17 g (11.6 mmol) of triethylamine. After 2 hours stirring at r.t., all volatiles were removed in vacuo, and 30 mL of toluene was added to the remaining solid. Filtration gave a clear solution, from which **4** crystallized upon storage at −18°C after 18 hours. Yield: 1.8 g (59.7%); m.p. 142°C. ^{1}H NMR (CDCl$_3$): δ = 7.12–7.39 [m, 15 H, C(C$_6$H$_5$)$_3$]. ^{31}P NMR (CDCl$_3$): δ = 208.5 [s]. C$_{25}$H$_{15}$Cl$_4$O$_2$P (520.18): calcd: C, 57.73; H, 2.91. Found: C, 57.77; H, 3.02.

Treatment of **4** *with HX (X = F, Cl).* Solutions of 0.06 g (0.12 mmol) of **4** in 0.5 mL of deuterochloroform were placed in 5 mm NMR tubes and treated at r.t. with (a) 0.02 g (0.12 mmol) of $NEt_3 \cdot 3\,HF$ and (b) 0.3 mL of a 1 M solution of HCl in diethyl ether. While ^{31}P NMR spectroscopy revealed that no reaction had taken place in the case of HCl, even after 18 hours, the following compounds were observed by ^{31}P NMR in the case of HF already after 15 minutes: $\delta = -12.7$ [dd, $^1J(PF) = 883.1$ Hz, $^1J(PH) = 818.2$ Hz, 10%, **2a**], 192.0 [d, $^1J(PF) = 1183.0$ Hz, 40%, **3a**], 208.5 [s, 50%, **4**].

*Triphenylmethyl-bis-(3,4,5,6-tetrachloro-1,2-phenylenedioxa)phosphorane (***5***).* (a) A solution of 0.50 g (1.7 mmol) of triphenylmethylfluorophosphine **1a** and 0.84 g (3.4 mmol) of TOB in 5 mL of dichloromethane was stirred at r.t. for 1 hour. Subsequently, the colorless precipitate was collected by filtration, washed with 5 mL of diethyl ether, and dried in vacuo. Yield: 1.01 g (77.6%); m.p. 207°C (dec.). ^1H NMR ($CDCl_3$): $\delta = 7.12$–7.46 [m, 15 H, $C(C_6H_5)_3$]. ^{31}P NMR ($CDCl_3$): $\delta = 2.4$ [s]. $C_{31}H_{15}Cl_8O_4P$ (766.05): calcd: C, 48.61; H, 1.97. Found: C, 48.37; H, 1.95. (b) A solution of 0.25 g (0.8 mmol) of triphenylmethylchlorophosphine **1b** and 0.40 g (1.6 mmol) of TOB in 4 mL of dichloromethane was stirred at r.t. for 1 hour. Subsequently, the colorless precipitate was collected by filtration, washed with 5 mL of diethyl ether, and dried in vacuo. Yield: 0.51 g (82.7%); m.p. 208°C (dec.).

X-RAY STRUCTURE DETERMINATION

Crystal Data. $C_{25}H_{15}Cl_4O_2P$, M = 520.14, triclinic, space group $P\bar{1}$, $a = 946.43(12)$, $b = 972.14(10)$, $c = 1231.92(10)$ pm, $\alpha = 89.569(8)°$, $\beta = 81.564(8)°$, $\gamma = 85.682(8)°$, $V = 1.1180(2)$ nm^3, $Z = 2$, $D_X = 1.545$ Mg m^{-3}, $\lambda(MoK_\alpha) = 71.073$ pm, $\mu = 0.62$ mm^{-1}, F(000) = 528, T = −100°C.

Data Collection and Reduction. A colorless prism 0.55 × 0.25 × 0.20 mm was mounted on a glass fiber in inert oil and transferred to the cold gas stream of the diffractometer (Siemens P4 with LT-2 low temperature attachment). In the 2θ range 6–50°, 3972 intensities were registered, of which 3936 were independent ($R_{int} = 0.016$). The cell constants were refined from setting angles of 65 reflections in the 2θ range 5–25°.

Structure Solution and Refinement. The structure was solved by direct methods and refined anisotropically on F^2 (program system: SHELXL-93, G.M.Sheldrick, University of Göttingen). H atoms were included using a riding model. The weighting scheme was of the form $w^{-1} = [\sigma^2(F_o^2) + (aP)^2 + bP]$, with $P = (F_o^2 + 2F_c^2)/3$. The final R(F) value was 0.031, with wR(F^2) = 0.070 for all reflections. S = 0.95; max $\Delta/\sigma < 0.001$; max $\Delta\rho = 230$ e.nm^{-3}.

Full details of the crystal structure determination (except structure factors) have been deposited under the number 111692 at the Cambridge Crystallographic Data Centre. Copies may be obtained free of charge from: The Director, CCDC, 12 Union Road, GB-Cambridge CB2 1EZ (Telefax: Int. + 1223/336-033; E-mail: deposit@ccdc.cam.ac.uk).

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