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# Reaction of 4,4´-dimethyldiphenyl ether with phosphorus trichloride in the presence of anhydrous aluminum chloride

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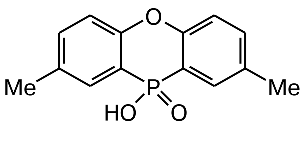
The reaction of 4,4´-dimethyldiphenyl ether with phosphorus trichloride in the presence of anhydrous aluminum chloride was studied. This reaction affords 2,8-dimethyl-10*H*-10λ$^5$-phenoxaphosphine 10-oxide as virtually the only product. In air, the latter in an alkaline solution is quantitatively transformed into 10-hydroxy-2,8-dimethyl-10*H*-10λ$^5$-phenoxaphosphine 10-oxide.

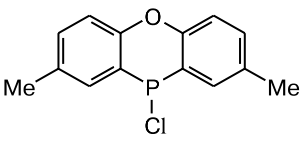
**Key words:** 4,4´-dimethyldiphenyl ether, phosphorylation of aromatic compounds, phosphorus trichloride, 2,8-dimethyl-10*H*-10λ$^5$-phenoxaphosphine 10-oxide.

Polyheteroarylenes are of great interest as thermally stable and heat- and fire-resistant systems,[1] matrices for catalyst immobilization, and solid electrolytes for proton-conducting membranes.[2] One of promising classes of polyheteroarylenes[3] includes aromatic polybenzimidazoles based on dicarboxylic acids and tetramines.[4—7] The aim of the present study was to synthesize new types of polybenzimidazoles containing hydroxyphosphoryl fragments chemically bound to the polymer chain. It should be noted that the attachment of the P atom through P—C bonds is optimal for providing high chemical and thermal stability of such polymers,[8] and the system can be additionally stabilized if the P atom is simultaneously involved in a fused aromatic heterocycle.

Taking into account the data presented in the monograph,[9] it can be concluded that 10-hydroxy-2,8-dimethyl-10*H*-10λ$^5$-phenoxaphosphine 10-oxide (**1**) (after its oxidation to the corresponding dicarboxylic acid) is the most interesting phosphorus-containing fused heterocyclic system suitable for the construction of hydroxyphosphoryl-containing polybenzimidazoles. Earlier,[10] it has been demonstrated that compound **1** can be prepared in high yield from readily available compounds, such as $PCl_3$, $AlCl_3$, and 4,4´-dimethyldiphenyl ether. It has been suggested[10] that intramolecular Friedel—Crafts cyclization initially affords acid chloride **2** followed by its oxidation to acid chloride of pentavalent phosphorus, whose hydrolysis gives compound **1**.



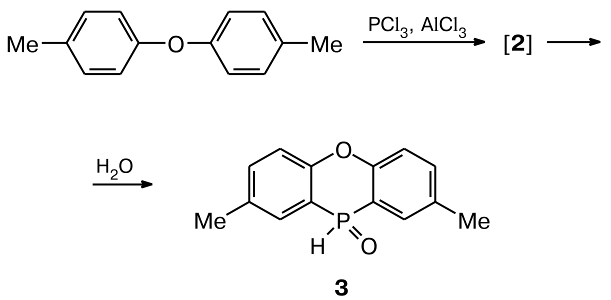
**1**



**2**

However, we found that the Friedel—Crafts reaction followed by hydrolysis of the reaction mixture under the conditions, which were completely identical to those described earlier,[10] afforded 2,8-dimethyl-10*H*-10λ$^5$-phenoxaphosphine 10-oxide (**3**) (Scheme 1) rather than phosphinic acid **1**. Compound **3** was isolated in 84% yield. Therefore, the results of our investigation reject the assumption of the intermediate formation of phosphoric acid chloride.

**Scheme 1**



Phosphine oxide **3** was prepared as a white powder, which does not melt up to 300 °C. Its structure was confirmed by elemental analysis and NMR spectroscopy ($^1$H, $^{31}$P, and $^{31}$P{$^1$H}). The $^1$H NMR spectrum has a doublet at δ 8.50 with the spin-spin coupling constant of 527.4 Hz. Since the virtually identical constant is observed in the $^{31}$P NMR spectrum (see the Experimental section), this signal can be assigned with certainty to the proton of the P—H fragment of molecule **3**. Phosphine oxide **3** is rather stable to atmospheric oxygen both in the solid state and in organic solvents (for example, in DMSO), but it is

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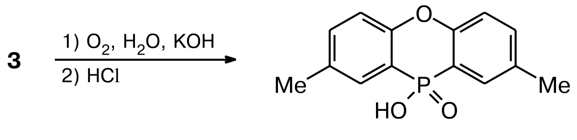
very rapidly oxidized upon treatment with an aqueous KOH solution in air to give hydroxyphosphine oxide **1** (Scheme 2).

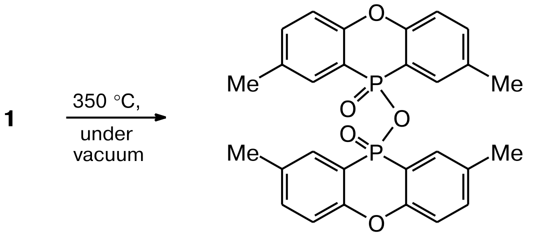
**Scheme 2**



**1** (92%)

The structure of compound **1** was also confirmed by elemental analysis and NMR spectroscopy ($^1$H and $^{31}$P{$^1$H}). The $^1$H NMR spectrum shows a broad singlet at δ 4.75 belonging to the proton of the P—OH group instead of a doublet for the proton of P—H. Compound **1** is stable in air up to 300 °C.* At temperatures higher than 350 °C, compound **1** is dehydrated *in vacuo* to form pyrophosphinate **4** (Scheme 3).

**Scheme 3**



**4**

In air, anhydride **4** is rapidly hydrolyzed to give again the starting compound **1**. This process occurs much more extensively in water-containing polar organic solvents.

The structure of anhydride **4** was established by X-ray diffraction analysis. Both phosphorus-containing heterocycles in pyrophosphinate **4** are planar, but their structures are slightly different (Fig. 1).** The phosphoryl group P(1)=O(1), unlike P(1´)—O(1´), is located above the plane of the adjacent phosphorus-containing ring. The shortest intramolecular O(1)...C(8) and O(1)...C(13) distances (3.071(2) and 3.128(2) Å, respectively) are slightly smaller than the sum of the corresponding van der Waals radii (3.31 Å). The O(1)—P(1)—P(1´)—O(1´) pseudotorsion angle is 163°. The dihedral angle between the planes of the rings is 128.4°.

The differences in the positions of the phosphoryl groups lead to changes in the bond lengths and, primarily, to elongation of the P(1´)—O(3) bond (1.628(2) Å) compared to the P(1)—O(3) bond (1.602(2) Å), the P(1)—O(1) bond being only slightly longer than the P(1´)—O(1) bond (Table 1).

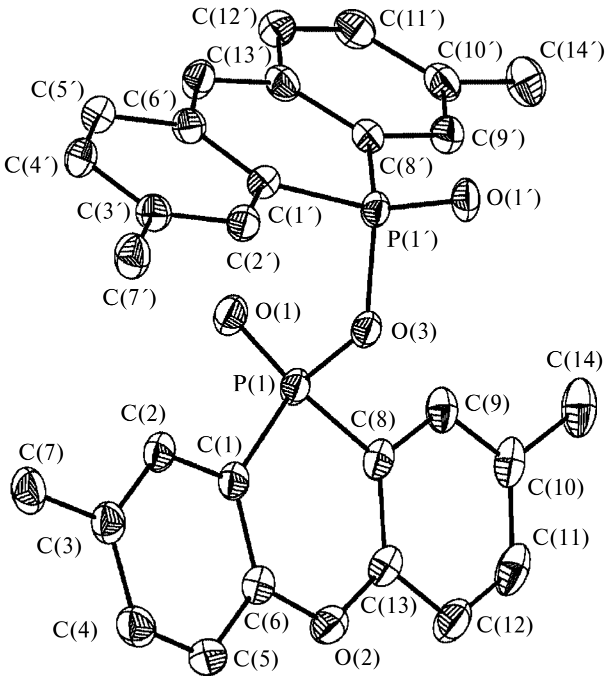


**Fig. 1.** Overall view of molecule **4** in the crystal. The H atoms are omitted.

Since the P atoms in the $^{31}$P{$^1$H} NMR spectrum of a solution of compound **4** are indistinguishable (singlet at δ 2.43), the phosphoryl groups are located, presumably, in *cis* positions.

**Table 1.** Selected bond lengths (*d*) and bond angles (ω) in the crystal of compound **4**

| Bond | *d*/Å | Bond | *d*/Å |
|---|---|---|---|
| P(1)—O(1) | 1.470(2) | P(1´)—O(3) | 1.628(2) |
| P(1)—O(3) | 1.602(2) | P(1´)—O(1´) | 1.460(2) |
| P(1)—C(1) | 1.764(3) | P(1´)—C(1´) | 1.753(3) |
| P(1)—C(8) | 1.760(3) | P(1´)—C(8´) | 1.767(3) |
| O(2)—C(6) | 1.367(4) | O(2´)—C(6´) | 1.375(4) |
| O(2)—C(13) | 1.372(4) | O(2´)—C(13´) | 1.366(4) |
| Angle | ω/deg | Angle | ω/deg |
| O(1)—P(1)—C(1) | 115.5(1) | O(1´)—P(1´)—O(3) | 107.0(1) |
| O(1)—P(1)—O(3) | 112.5(1) | O(1´)—P(1´)—C(1´) | 117.2(1) |
| O(1)—P(1)—C(8) | 117.0(1) | O(3)—P(1´)—C(1´) | 104.7(1) |
| O(3)—P(1)—C(1) | 104.9(1) | O(1´)—P(1´)—C(8´) | 117.1(1) |
| O(3)—P(1)—C(8) | 102.3(1) | O(3)—P(1´)—C(8´) | 106.6(1) |
| C(8)—P(1)—C(1) | 102.9(1) | C(1´)—P(1´)—C(8´) | 103.2(1) |
| C(13)—O(2)—C(6) | 123.5(2) | C(6´)—O(2´)—C(13´) | 123.7(2) |
| P(1)—O(3)—P(1´) | 132.0(1) | | |

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* Solutions of this compound in organic solvents are also stable.

** The P atoms in the heterocycles are characterized by a slightly distorted tetrahedral coordination with the intramolecular C—P—C angle decreased to 102.9(1)°.

Apparently, this conformation of molecule **4** is stabilized in the crystal due partially to stacking interactions between the aromatic rings. In the crystal structure, molecules **4** are linked to form centrosymmetric dimers through the C(1´)—C(14´) interaction of the ring with the shortest C...C distance of 3.360(2) Å. In addition to the stacking interactions, there is also a rather strong C—H...O contact, *viz*., P(1´)—O(1´)...H(14E)—C(14´) (H...O, 2.18 Å; C—H—O, 169°), through which the dimers are linked to each other to form layers parallel to the crystallographic plane *bc*.

## Experimental

The $^1$H and $^{31}$P NMR spectra were recorded on a Bruker AMX-400 instrument (400.13 and 161.98 MHz, respectively) in DMSO-d$_6$. The chemical shifts δ were calculated with respect to the residual signals for the protons of the deuterated solvent as the internal standard ($^1$H) and 85% $H_3PO_4$ as the external standard ($^{31}$P). The melting points were measured on a Boetius hot-stage apparatus and are uncorrected. The course of the reactions and the purity of the reaction products were monitored by TLC on Silufol UV-254 plates using a $PhCH_3$—MeOH mixture as the eluent. Phosphorus trichloride (ReaKhim) was purified by distillation, and aluminum chloride (ReaKhim) was sublimed under vacuum at 300 °C. 4,4´-Dimethyldiphenyl ether (Donetsk Plant of Chemical Reagents) was characterized by m.p. 49—52 °C .

**2,8-Dimethyl-10*H*-10λ$^5$-phenoxaphosphine 10-oxide (3).** Anhydrous freshly sublimed $AlCl_3$ (8.5 g, 0.064 mol), 4,4´-dimethyldiphenyl ether (9.9 g, 0.05 mol), and freshly distilled $PCl_3$ (27.4 g, 0.2 mol) were placed in a round-bottom flask equipped with a reflux condenser and a calcium chloride tube. The reaction mixture was heated at 80 °C for 22 h. The oily product was poured onto ice. After 3—4 h, the precipitate that formed was separated, washed with distilled water to neutral pH, and dried in a vacuum desiccator at 100 °C for 4 h to prepare compound **3** in a yield of 10.2 g (84%), m.p. > 300 °C. Found (%): C, 68.54; H, 5.64; P, 12.54. $C_{14}H_{13}O_2P$. Compound (%): C, 68.85; H, 5.36; P, 12.68. $^1$H NMR (DMSO-d$_6$), δ: 2.40 (s, 6 H, Me); 7.33 (dd, 2 H, H(4), H(6), $^3J_{H,H}$ = 8.6 Hz, $^4J_{H,P}$ = 6.2 Hz); 7.57 (dd, 2 H, H(3), H(7), $^3J_{H,H}$ = 8.8 Hz, $^4J_{H,H}$ = 1.6 Hz); 7.75 (dd, 2 H, H(1), H(9), $^3J_{H,P}$ = 14.0 Hz, $^4J_{H,H}$ = 1.6 Hz); 8.50 (d, 1 H, PH, $^1J_{H,P}$ = 527.4 Hz). $^{31}$P NMR (DMSO-d$_6$), δ: –16.24* (dtt, $^1J_{H,P}$ = 527.7 Hz, $^3J_{P,H}$ = 14.0 Hz, $^4J_{H,P}$ = 6.1 Hz).

**10-Hydroxy-2,8-dimethyl-10*H*-10λ$^5$-phenoxaphosphine 10-oxide (1).** Phosphine oxide **3** (10.0 g, 0.04 mol) was dissolved in a minimum volume of a 10% aqueous KOH solution. The solution was filtered, and the filtrate was acidified with concentrated HCl to pH 2. The precipitate that formed was separated, washed with distilled water to pH 7, and dried in a vacuum desiccator at 100 °C for 6 h to prepare compound **1** in a yield of 9.80 g (92%), m.p. > 300 °C. Found (%): C, 64.67; H, 5.04; P, 11.95. $C_{14}H_{13}O_3P$. Compound (%): C, 64.62; H, 5.03; P, 11.90. $^1$H NMR (DMSO-d$_6$), δ: 2.38 (s, 6 H, Me); 4.75 (br.s, 1 H, OH); 7.26 (dd, 2 H, H(4), H(6), $^3J_{H,H}$ = 8.0 Hz, $^4J_{H,P}$ = 7.2 Hz); 7.46 (d, 2 H, H(3), H(7), $^3J_{H,H}$ = 8.4 Hz); 7.59 (d, 2 H, H(1), H(9), $^3J_{H,P}$ = 13.6 Hz). $^{31}$P{$^1$H} NMR (DMSO-d$_6$), δ: 3.56 s.

**2,8-Dimethyl-10-[(2,8-dimethyl-10-oxo-10*H*-10λ$^5$-phenoxaphosphin-10-yl)oxy]-10*H*-10λ$^5$-phenoxaphosphine 10-oxide (4)** was prepared in quantitative yield by vacuum sublimation of compound **1** at 350 °C. M.p. > 350 °C. $^{31}$P{$^1$H} NMR (DMSO-d$_6$), δ: 2.43 c.

**X-ray diffraction study of phosphine oxide 4** ($C_{28}H_{24}O_5P_2$) was carried out on an automated three-circle Smart CCD diffractometer (Mo-Kα radiation, graphite monochromator, ω scanning technique, $2\theta_{max}$ = 52°). Crystals at 110 K are triclinic, $a$ = 8.391(3) Å, $b$ = 9.758(4) Å, $c$ = 15.684(6) Å, α = 100.535(9)°, β = 100.663(9)°, γ = 108.580(9)°, $V$ = 1155.2(8) Å$^3$, $d_{calc}$ = 1.444 g cm$^{-3}$, M = 502.41, $F$(000)= 524, μ = 2.28 cm$^{-1}$, $Z$ = 2, space group $P\bar{1}$. Of a total of 5900 measured reflections, 4142 independent reflections ($R_{int}$ = 0.0263) were used in subsequent calculations and refinement. The structure was solved by direct methods and refined by the full-matrix least-squares method with anisotropic displacement parameters for nonhydrogen atoms against $F^2_{hkl}$. The H atoms were revealed from difference Fourier syntheses and refined using a riding model. The final reliability factors were as follows: $wR_2$ = 0.1392, GOF = 1.092 using all reflections ($R$ = 0.0600 based on 3174 reflections with $I > 2\sigma(I)$). All calculations were carried out on IBM-PC/AT using the SHELXTL PLUS program package.

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* The $^{31}$P NMR spectrum measured with proton noise decoupling shows a singlet instead of this multiplet.