Halogenation of 1-Ethoxy-1-oxophosphindolin-3-one, a Potential Phosphaindigo Precursor

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The bromination of 1-ethoxy-1-oxophosphindolin-3-one (**1**) with two equivalents of bromine occurs with elimination of hydrogen bromide and ethyl bromide, providing 2,2-dibromo-1-hydroxy-1-oxophosphindolin-3-one (**4**) in high yield. In the presence of triethylamine this process leads to 2,2-dibromo-1-ethoxy-1-oxophosphindolin-3-one (**3**) instead. Triethylamine deprotonates **4**, providing the solid triethylammonium salt **5**. Silylation of **4** with chlorotrimethylsilane leads to the trimethylsilyl ester **6**. Monobromination in a two-phase reaction allows the isolation of a mixture of isomers of 2-bromo-1-ethoxy-1-oxophosphindolin-3-one (**2a**, **b**). Chlorination with chlorine furnishes 2,2-dichloro-1-ethoxy-1-oxophosphindolin-3-one (**7**). The new compounds **2**−**7** were characterized analytically and spectroscopically (EI-MS; ^{1}H, ^{13}C and ^{31}P NMR). The crystal structure of acid **4** was determined by X-ray diffraction. Solid **4** consists of aryl stacks connected by chains of P−OH···O=P hydrogen bonds and secondary Br···Br contacts.

The substitution of a methine (=CH−) group by a phosphorus atom in the polymethine chain of cyanine dyes was a milestone in the chemistry of colorants[1]. Since then the chemistry of low-coordinated phosphorus, including species with conjugated P=C and C=C bonds[2][3], has been developed far beyond the classic phosphabenzene syntheses of Märkl[4]and Ashe[5]. The search for novel compounds with phosphorus atoms participating in π-conjugation has also led to the synthesis of a number of five-membered phosphorus heterocycles, among them the pentaphosphacyclopentadienide anion[6] and tetraphosphafulvalenes[7]. However, a great challenge in the chemistry of both π-conjugated organophosphorus compounds and dyestuffs remains: the preparation of phosphaindigo, in which the three-coordinated nitrogen of the amino group of indigo is replaced by phosphorus.

To make predictions about the light absorption of phosphaindigo derivatives possible, the electronic absorption bands of some indigoids were calculated by PM3/CI (Table 1)[8]. It turns out that phosphaindigos **II** and **IV** should absorb at considerably shorter wavelengths than the parent systems **I** and **III**. Concerning structural features of **II** and **IV**, the calculations predict pyramidalization of the C_2PH moieties and weak hydrogen-bond-like interactions between the P−H and carbonyl groups[8]. These predictions agree with the results from studies that indicate poor π-overlap between pyramidal phosphorus atoms and adjacent carbon atoms of phospholes. Flattening of phosphorus with help from sterically demanding substituents, however, is accompanied by strong electron delocalisation[9]. As alternative approach to delocalisation deprotonation of phosphaindigo derivatives **II** might lead to 1-phosphaallyl-type anions **VI**, which are closely related to thioindigo **V**, whose light absorption indicates significant p−p π-overlap between sulfur and the adjacent carbon atoms[10].

There are still no experimental data on the synthesis and properties of phosphaindigo **II** and its anion **VI**. In order to obtain phosphaindigo **II** and compare its properties with predictions, we have planned a systematic approach. The crucial steps of the syntheses of indigo-related dyes are oxidative coupling reactions of indole-related precursors. Here we report our first synthetic steps towards the oxidation of phosphaindigo precursors leading to new phosphaindanone ("phosphindole") derivatives. Indole-related benzophosphole ("phosphindole") derivatives are well known but only scattered infomation is available on their 3-oxo derivatives[11], which would be related to precursors of indigo **I** or thioindigo **V**.

Reactions

3-Oxophospholes exist predominantly in their enol forms[12][13], whereas the "benzophosphole derivative" 1-ethoxy-1-oxophosphindolin-3-one (**1**) shows a notable preference for the keto form[11]. As a C−H acidic compound, **1** is easily deprotonated by bases[11]. The enolate is known to react with acyl chlorides by *O*-acylation, whereas with isocyanates C−C coupling reactions occur, followed by extraction with HCl/CH_2Cl_2 to furnish stable enols[11]. Reports on oxidation reactions with **1** have to the best of our knowledge not yet been published. Mild oxidizing agents

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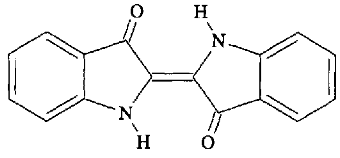
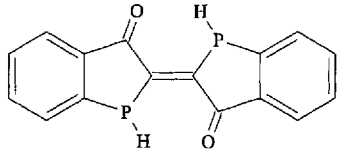
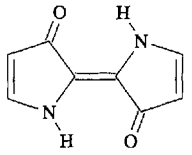
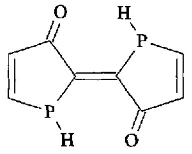
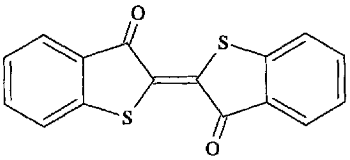
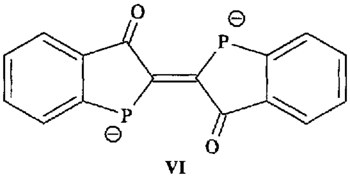
Table 1. Calculated longest wavelength absorption maxima of indigoid dyes **I**–**IV**

Molecule	Calcd. λ_{max} [nm]
 I	426
 II	347
 III	453
 IV	356

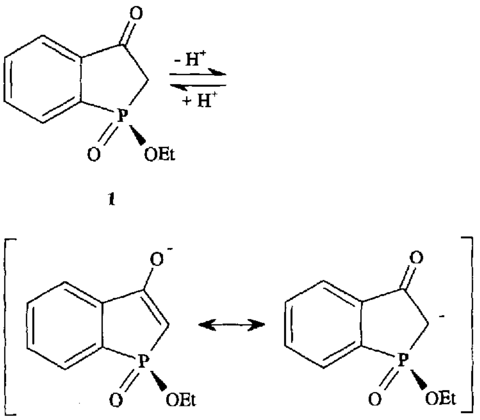


V



VI

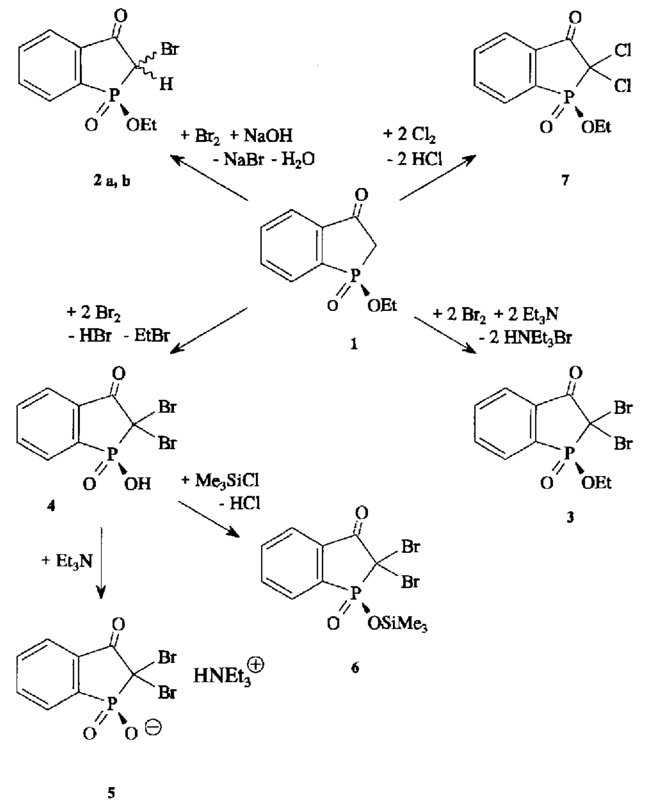
such as $K_3Fe(CN)_6$, which would oxidize related indole derivatives or sulfur heterocycles to indigo or thioindigo, did not induce oxidative C=C coupling in the case of **1** or its anion[15].



To elucidate whether the oxidation of 1-hydroxy-1-oxophosphindolin-3-one (**1**) with stronger oxidants would lead to C–C or C=C coupling, related to the formation of known heteroindigo derivatives, we studied the reactions of **1** with molecular bromine, chlorine and iodine. The reaction of **1** with molecular bromine under varied conditions was monitored by ^{31}P-NMR spectroscopy. The desired oxidative C=C coupling of **1** or its anion was not observed in any of these experiments. Treatment of **1** with less than two equivalents of bromine gave mixtures of the stereoisomers of the monobromo derivatives **2a**, **b** (^{31}P: $\delta = 33.2$ and 34.6) and the dibromo product **3** (^{31}P: $\delta = 27.8$). These mixtures also contained increasing amounts of substances such as **4** (^{31}P: $\delta = 24.3$), which were generated by cleavage of the P–OEt ester function. After addition of two equivalents of bromine to a trichloromethane solution of **1**, the phosphinic acid derivative **4** precipitated in high yield as a yellow solid, only sparingly soluble in trichloromethane and dichloromethane. NMR spectra of **4** can be recorded in D_2O/dioxane and tetrahydrofuran, whereas acetone is best suited for recrystallizations of **4**. The influence of the solvent according to the NMR shift is rather large. The ^{31}P-NMR chemical shifts of **1** vary from $\delta = 49.1$ (D_2O) to 40.9 (benzene).

The dealkylation with the in situ formed hydrogen bromide can largely be suppressed by carrying out the bromination in the presence of excess triethylamine. Hydrogen bromide from the *C*-bromination reaction is removed by triethylamine to form triethylammonium bromide. Under these conditions, 2,2-dibromo-1-ethoxy-1-oxophosphindolin-3-one (**3**) was obtained in up to 70% yield. However, yields of **3** from individual batches varied from about 30 to 70% due to the formation of varying amounts of **4** or its triethylammonium salt **5**. The triethylammonium salt **5** is obtained by addition of an excess of triethylamine to a solution of the acid **4** in tetrahydrofuran. Crystallization from tetrahydrofuran furnishes pure **5** in fair yield as colorless solid. Silylation of **4** leading to the trimethylsilyl ether **6** was achieved by heating the phosphinic acid with an excess of chlorotrimethylsilane. The silyl compound **6** was obtained in high yield as a yellowish oily liquid.

To prepare the pure monobromo derivatives **2a**, **b** of the phosphinic ester **1**, it was necessary to avoid a local excess of bromine (leading to **3**) and the presence of anhydrous hydrogen bromide leading to P–OEt cleavage. To suppress "hydrolysis" of the P–OEt group, it proved helpful to use aqueous sodium hydroxide for the removal of HBr. For this purpose, the bromination was carried out in a two-phase system. Adding one equivalent of bromine in dichloromethane to deprotonate **1** in aqueous sodium hydroxide avoided dibromination and hydrolysis that would give **3** and **4** and/or **5**. After acidification of the reaction mixture, the mixture of monobromo products **2a**, **b** was isolated from the di-



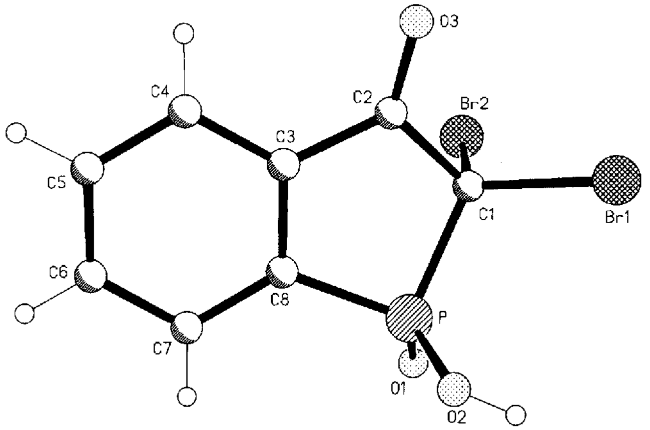
chloromethane phase; crystallization from diethylether furnished **2a, b** as a white solid.

Because silylation of **4** with an excess of chlorotrimethylsilane, to furnish **6**, under liberation of gaseous hydrogen chloride) proceeded straightforwardly without significant cleavage of the P–OEt ester group, we concluded that phosphinic ester **1** and its derivatives **2**, **3** are easily cleaved by anhydrous HBr, but not by HCl, the weaker acid. Therefore chlorination of **1** with molecular chlorine under anhydrous conditions should proceed with liberation of HCl gas without ester cleavage. Indeed, bubbling an excess of molecular chlorine through a CH_2Cl_2 solution of **1** led to chlorination in the 2-position. In contrast to the bromination of **1** (leading to phosphinic acid **4**), dichlorination of **1** was not accompanied by formation of significant amounts of products from the cleavage of the P–OEt bond. The chlorination provided 2,2-dichloro-1-ethoxy-1-oxophosphindolin-3-one (**7**) in modest yield. Molecular iodine did not react with **1** under the same reaction conditions.

The formulated structures of compounds **2**–**7** were confirmed analytically, by mass and NMR spectroscopy. Phosphinic acid **4** requires solvents with proton accepting properties; its ^{31}P signal appears only slightly upfield from the ester **3**. The ^{31}P resonance of the anion **5**, however, is found about 10 ppm further upfield from that of **4** (in THF). ^{13}C resonances do not follow this trend (Table 2). All carbon nuclei of the phosphindole ring system exhibit spin-spin coupling with the ^{31}P nucleus. The experimental isotopic patterns of the molecular ions of all compounds are in good agreement with calculations.

A crystal-structure determination confirmed the nature of **4**. The endocyclic angle at phosphorus (C1–P–C8) is small (93.2°), with a resulting large exocyclic O1–P–O2 angle (117.2°). The torsion angles within the $-PO_2-CBr_2-$ moieties of **4** allow the nonequivalent O atoms and Br atoms to be classified as "axial" (O2, Br2: significantly out of the ring plane) and "equatorial" (O1, Br1: slightly out of the ring plane, see Figure 1). Angles C2–C1–Br2 (105.7°) and P–C1–Br(2) (108.1°) are larger than the corresponding angles involving the other bromine atom (C2–C1–Br1 112.1°, P–C1–Br1 114.7°): "equatorial" Br1 is closer to the plane of the adjacent 5-membered ring and is also bonded more tightly (C1–Br1 192.0 pm) than the other ("axial") bromine atom (C1–Br2 196.1 pm).

Figure 1. Molecular structure of **4**; selected bond lengths [Å] and angles [°][a]



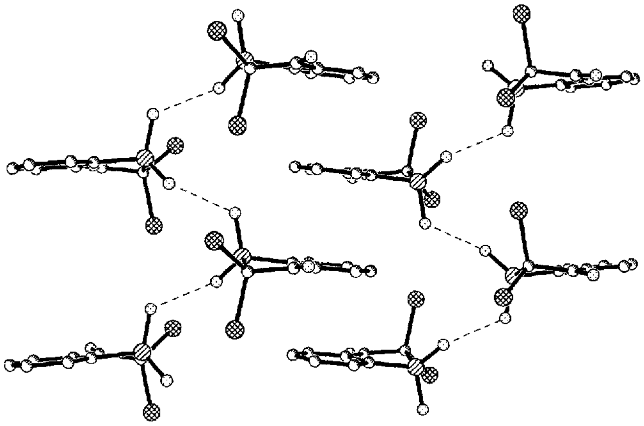
[a] P–C1 1.839(5), P–C8 1.774(4), P–O1 1.483(3), P–O2 1.532(3), C1–Br1 1.920(4), C1–Br2 1.961(4); C1–P–C8 93.2(2), C1–C2–C3 110.0(4), Br1–C1–P 114.7(2), Br2–C1–P 108.1(2).

The packing diagrams of **4** reveal that three types of intermolecular interactions contribute to the extended network: "hard" hydrogen bonding, "soft" bromine–bromine attraction, and aromatic π-stacking. As in known dimeric or helical structures of phosphinic acids[16][17], intermolecular hydrogen bridging P–O(2)–H···O(1′)=P′ leads to a slight lengthening of P=O(1) (146.7 pm, decrease of the double-bond character) and a slight shortening of P–O2 (153.2 pm, compared to a typical P–O single-bond length of 159 pm[16][17]). P–O–H···O=P hydrogen bonding in **4** leads to slightly helical zigzag chains (Figure 1)[17][18]. The strands from this type of intermolecular interaction are interconnected by strands of intermolecular Br2···Br1′ contacts of ca. 370 pm (Figure 3) leading to a crisscross three-dimensional network of weak interactions (Figure 1). The orientation of the intermolecular contacts is $P-O_{ax}-H\cdots O=P_{eq}$ and $Br_{ax}\cdots Br_{eq}$. The carbonyl group in the 3-position is not involved in this network. The aryl groups of each second unit of two adjacent $P-O_{ax}-H\cdots O_{eq}-P$ chains build up linear stacks of essentially coplanar aromatic rings (Figure 2). Cooperative contributions from hydrogen bonding, "soft-soft" ($Br_{ax}\cdots Br_{eq}$) interactions[19] and aromatic stacking make **4** a rather high-

Table 2. Selected NMR data of compounds **1**–**7**

Compound R	**1** 2-H_2 Et	**4** 2-Br_2 H	**3** 2-Br_2 Et	**5** 2-Br_2 Et	**6** 2-Br_2 $SiMe_3$	**7** 2-Cl_2 Et	**2a**, **2b** 2-H, 2-Br Et
δ ^{13}C (J[PC])							
C-2	35.7 (101.3)	54.6 (88.6)	50.4 (94.0)	50.4 (94.0)	50.2 (102.4)	71.9 (106.6)	37.1, 39.3 (101.2, 97.7)
C-3	192.5 (19)	191.0 (25.1)	185.0 (26.4)	185.0 (26.4)	184.8 (27.7)	184.1 (29.8)	188.1, 188.7 (22.4, 23.9)
C-8	139.2 (119.5)	138.9 (129.3)	133.2 (133.2)	141.0 (128.4)	134.0 (135.0)	134.3 (134.3)	136.0, 136.2 (127.2, 126.7)
C-9	141.1 (15.8)	133.3 (11.6)	135.4 (12.1)	134.0 (11.1)	134.2	135.6 (12.1)	138.7, 139.0 (14.3, 14.2)
C-10	62.3 (6.6)		64.9 (6.9)	45.8	1.1; 3.1 [$SiMe_3$]	65.1 (6.9)	63.6, 64.0 (6.5, 6.9)
C-11	16.4 (6.3)		16.4 (6.1)	8.7		16.3 (6.0)	16.2, 16.3 (6.8, 6.1)
δ ^{31}P	42.9	24.7	27.8	16.7	18.5	28.7	33.2, 34.6

Figure 2. Packing diagram of **4**; H atoms are omitted for clarity[a]



[a] Hydrogen bonds between O2 and O1′ [Å; °]: O2–O1′ 2.473(4), H2–O1′ 1.668(6); O2–H2–O1′ 159.6(11); symmetry operator for generating equivalent atom O1′: $-x + 0.5, y + 0.5, -z + 1.5$.

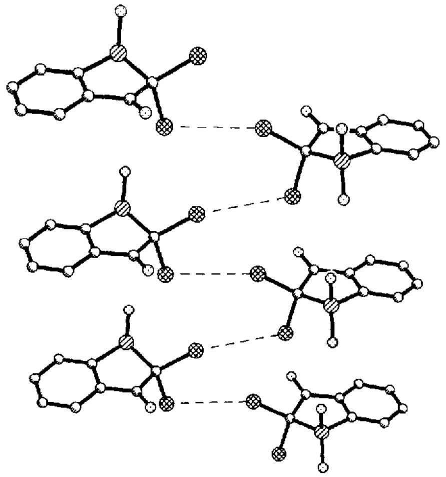
melting compound that is nearly unsoluble in hydrocarbon solvents.

The triethylammonium salt **5** has a relatively high solubility and low melting point; the solid consists of ion pairs with N-H···O hydrogen bonding between (severely disordered) triethylammonium cations and phosphinate anions.

Experimental Section

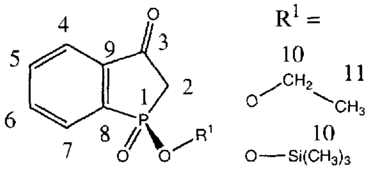
^1H-, ^{13}C- and ^{31}P-NMR spectra were recorded with a Bruker AM 200 (200.1, 50.3, and 81.0 MHz, respectively) using $CDCl_3$ (TMS as internal reference) as solvent, if not otherwise specified. J values are given in Hz. The degree of substitution of the carbon atoms was determined by DEPT-135° experiments. Further assignments were made with the help of CH correlation and COLOC spectra (indicated in the ^{13}C-NMR assignments by superscript CHC or COL, respectively). – EI mass spectra were recorded with a Finnigan MAT 8430 spectrometer operating at 70 eV. – FAB MS (pos) were recorded with a Finnigan MAT 8340 spectrometer. 3-Nitrobenzyl alcohol (NBA) was used as liquid matrix. – Melting points were determined with a Kofler hot stage microscope and all values are uncorrected. – Elemental analyses were carried out by the Analytisches Laboratorium des Instituts für Anorganische und Analytische Chemie, Technische Universität Braunschweig. – Separations by column chromatography were performed on 70–230 mesh silica gel from Merck, Darmstadt. – In all reactions requiring anhydrous conditions solvents were dried by distillation under nitrogen from the appropriate drying agent, glassware was flame-dried and cooled afterwards under a steady stream of nitrogen. – Numbering of the carbon and phosphorus nuclei of **2** and its derivatives are shown in Figure 4.

Figure 3. Packing diagram of **4**; H atoms are omitted for clarity[a]



[a] Bromine–bromine interactions: Br1–Br2′ 3.706(1) Å; symmetry operator for Br2′: $-x + 1.5, y + 0.5, -z + 1.5$.

Figure 4. Numbering of the carbon and phosphorus nuclei of **2** and its derivatives



2-Bromo-1-ethoxy-1-oxophosphindolin-3-one (**2a**, **b**): To a solution of **1** (1.9 g, 9.0 mmol) in CH_2Cl_2 (50 ml) was added a solution of NaOH (1.2 g, 30.0 mmol). A solution of bromine (1.44 g, 9.0

mmol) in CH_2Cl_2 (10 ml) was added dropwise to this mixture. After stirring for 15 min, the reaction mixture was acidified with dilute hydrochloric acid. Then the phases were separated and the organic phase was extracted three times with CH_2Cl_2 (30 ml). The combined organic phases were dried with sodium sulphate and then the solvents were removed. The oily residue was dissolved in diethyl ether and then placed in a refrigerator to yield **2** (3.0 g, 90%) as white solid mixture of isomers, m.p. 75°C. – ^{1}H NMR: δ = 1.2 (2 t), 4.2 (m, 2 H, 10-H), 4.43 [d, ^2J(H,P) = 8.6 Hz, 1 H, 2-H], 4.64 [d, ^2J(H,P) = 11.6 Hz, 1 H, 2-H], 7.7 (m, 4 H, H-Ar). – ^{13}C NMR: δ = 16.2 [d, ^3J(C,P) = 6.8 Hz, C-11], 16.3 [d, ^3J(C,P) = 6.1 Hz, C-11], 37.1 [d, ^1J(PC) = 101.2 Hz, C-2], 39.3 [d, ^1J(PC) = 97.7 Hz, C-2], 63.6 [d, ^2J(C,P) = 6.5 Hz, C-10], 64.0 [d, ^2J(C,P) = 6.9 Hz, C-10], 124.9 [d, ^3J(C,P) = 12.9 Hz, C-6], 125.2 [d, ^3J(C,P) = 13.1 Hz, C-6], 127.8 [d, ^2J(C,P) = 5.0 Hz, C-7], 128.1 [d, ^2J(C,P) = 4.7 Hz, C-7], 134.2 [d, ^4J(C,P) = 2.5 Hz, C-5], 134.3 [d, ^4J(C,P) = 2.6 Hz, C-5], 136.0 [d, ^1J(C,P) = 127.2 Hz, C-8], 136.1 [d, ^3J(C,P) = 12.3 Hz, C-4], 136.2 [d, ^1J(C,P) = 126.7 Hz, C-8], 138.7 [d, ^2J(C,P) = 14.3 Hz, C-9], 139.0 [d, ^2J(C,P) = 14.2 Hz, C-9], 188.1 [d, ^2J(C,P) = 22.4 Hz, C-3], 188.7 [d, ^2J(C,P) = 23.9 Hz, C-3]. – ^{31}P NMR: δ = 34.6 (s), 33.2 (s). – EI MS; *m/z* (%): 288 (92) [M$^+$], 260 (100), 244 (44). – $C_{10}H_{10}BrO_3P$ (289.1): calcd. C 41.55, H 3.49; found C 41.68, H 3.64.

2,2-Dibromo-1-ethoxy-1-oxophosphindolin-3-one (**3**): To a stirred solution of (3.0 g, 14.3 mmol) **1** and triethylamine (4.0 ml, 28.6 mmol) in benzene (30 ml) was added dropwise a solution of bromine (4.55 g, 28.6 mmol) in benzene (15ml). After stirring for 30 min, diethyl ether (30 ml) was added. The precipitate was filtered off and extracted 3 times with 15 ml of diethyl ether. Then all volatiles were removed in vacuo. Recrystallization of the oily residue from diethyl ether yielded 3.7 g (71%, different batches: 30–70%) of **3** as a colorless solid, m.p. 125°C. – ^{1}H NMR (C_6D_6): δ = 0.9 (t, ^3J = 6.8 Hz, 3 H, CH_3), 4.2 (m, 2 H, CH_2), 6.9 (m, 2 H, 2,5-H), 7.4 (m, 1 H, 7-H), 7.6 (m, 1 H, 6-H). – ^{13}C NMR (C_6D_6): δ = 16.4 [d, ^3J(C,P) = 6.1 Hz, CH_3], 50.4 [d, ^1J(C,P) = 94.0 Hz, C-2], 64.9 [d, ^2J(C,P) = 6.9 Hz, CH_2], 126.5 [d, ^3J(C,P) = 6.0 Hz, C-6], 128.7 [d, ^2J(C,P) = 5.1 Hz, C-7], 133.2 [d, ^1J(C,P) = 133.2 Hz, C-9], 134.3 [d, ^4J(C,P) = 2.4 Hz, C-5], 135.4 [d, ^2J(C,P) = 12.1 Hz, C-9], 136.2 [d, ^3J(C,P) = 12.7 Hz, C-4], 185.0 [d, ^2J(C,P) = 26.4 Hz, C-3]. – ^{31}P NMR (C_6D_6): δ = 27.8 (s). – EI MS; *m/z* (%): 368 (45) [M$^+$], 340 (100). – $C_{10}H_9Br_2O_3P$ (367.9) calcd. C 32.64, H 2.47; found C 32.58, H 2.44.

2,2-Dibromo-1-hydroxy-1-oxophosphindolin-3-one (**4**): To a stirred solution of phosphindolin-3-one **1** (4.3 g, 20.4 mmol) in $CHCl_3$ (20 ml) was added dropwise a solution of bromine (8.5 g, 53.5 mmol) in $CHCl_3$ (15.2 ml). Subsequently, the stirrer was turned off and the product crystallized within about 20 min. The crystals were washed with diethyl ether and CH_2Cl_2. After drying in vacuo, 6.8 g (98%) **4** was isolated as a yellow solid, m.p. 235°C (acetone). Single crystals suitable for an X-ray structure determination were obtained from the trichloromethane mother liquor from the synthesis of **4**. – ^{1}H NMR ([D_8]THF): δ = 8.0 (m, 4 H, ArH), 10.9 (s, 1 H, OH). – ^{13}C NMR (D_2O/dioxane): δ = 54.6 [d, ^1J(C,P) = 88.7 Hz, C-2], 127.1 [d, ^3J(C,P) = 11.2 Hz, C-6], 128.0 [d, ^2J(C,P) = 5.2 Hz, C-7], 133.3 [d, ^2J(C,P) = 11.6 Hz, C-9], 133.9 [d, ^4J(C,P) = 2.2 Hz, C-5], 138.2 [d, ^3J(C,P) = 11.8 Hz, C-4], 138.9 [d, ^1J(C,P) = 129.3 Hz, C-8], 191.0 [d, ^2J(C,P) = 25.1 Hz, C-3]. – ^{31}P NMR (THF and a capillary with C_6D_6): δ = 24.7 (s). – EI MS; *m/z* (%): 340 (100) [M$^+$], 260 (14), 231 (14), 151 (42). – $C_8H_5Br_2O_3P$ (339.9): calcd. C 28.27, H 1.48; found C 28.36, H 1.52.

Triethylammonium Salt **5**: Triethylamine (0.3 ml, 2.2 mmol) was added to a stirred solution of **4** (0.5 g, 1.5 mmol) in 10 ml THF. By keeping the solution for 1 d at −18°C solid **5** (0.6 g, 93%) precipitated, m.p. 125°C; good solubility in polar solvents such as H_2O, EtOH, THF, $CHCl_3$, and CH_2Cl_2. Single crystals were grown from CH_2Cl_2/pentane.– ^{1}H NMR: δ = 1.35 (t, ^3J = 7.3 Hz, 9 H, CH_3), 3.1 (dq, ^3J = 4.7, ^3J = 7.3 Hz, 6 H, CH_3), 7.7 (m, 4 H, ArH), 11.7 (m, 1 H, NH). – ^{13}C NMR: δ = 8.6 (s, CH_3), 45.7 (s, CH_3), 58.0 [d, ^1J(C,P) = 82.4 Hz, C-2], 126.0 [d, ^3J(C,P) = 10.9 Hz, C-6], 127.4 [d, ^2J(C,P) = 5.3 Hz, C-7], 131.6 [d, ^4J(C,P) = 2.2 Hz, C-5], 134.0 [d, ^2J(C,P) = 11.1 Hz, C-9], 135.7 [d, ^3J(C,P) = 11.5 Hz, C-4], 141.0 [d, ^1J(C,P) = 128.4 Hz, C-8], 189.1 [d, ^2J(C,P) = 26.4 Hz, C-3].– ^{31}P NMR: δ = 16.7 (s).– FAB MS; *m/z* (%): neg: 338 (100) [anion], 258 (26); pos: 102 (100) [cation]. – $C_{14}H_{20}Br_2NO_3P$ (440.9): calcd. C 38.27, H 4.56, N 3.19; found C 38.50, H 4.69, N 3.31.

2,2-Dibromo-1-oxo-1-trimethylsiloxyphosphindolin-3-one (**6**): A suspension of 2,2-dibromo-1-hydroxy-1-oxophosphindolin-3-one (**4**) (0.8 g, 2.3 mmol), suspended in chlorotrimethylsilane (8 ml), was heated to 60°C until a clear solution had formed (about 30 min). Then the chlorotrimethylsilane was removed in vacuo to give 0.9 g (ca. 100%) of **6** as a yellow oily liquid, sensitive to moisture and reasonably soluble in hydrocarbons and ethers. – ^{1}H NMR: δ = 0.3 (s, 9 H, CH_3), 7.9 (m, 4 H, 4,5,6,7-H). – ^{13}C NMR: δ = 1.1, 3.1 (s, CH_3), 50.2 [d, ^1J (C,P) = 102.4 Hz, C-2], 126.6 [d, ^3J (C,P) = 12.2 Hz, C-6], 128.0 [d, ^2J (C,P) = 5.1 Hz, C-7], 134.0 [d, ^1J (C,P) = 135.0 Hz, C-8], 134.2 (d, C-9), 134.3 [d, ^4J (C,P) = 2.1 Hz, C-5], 136.6 [d, ^3J (C,P) = 12.8 Hz, C-4], 184.8 [d, ^2J (C,P) = 27.7 Hz, C-3]. – ^{31}P NMR: δ = 18.6 (s). – EI MS; *m/z* (%): 412 (0.8) [M$^+$], 340 (100). – This compound did not give a satisfactory microanalysis.

2,2-Dichloro-1-ethoxy-1-oxophosphindolin-3-one (**7**): Chlorine was bubbled for 15 min through a solution of **1** (0.8 g, 3.8 mmol) in dichloromethane (15 ml). After removal of the solvent and the excess of chlorine in vacuo, the residue was recrystallized from diethyl ether to yield 1.0 g (76.9%) of **7** as a colorless solid, m.p. 56°C. – ^{1}H NMR: δ = 1.3 (t, ^3J = 7.0 Hz, 3 H, 11-H), 4.4 (m, 2H, 10-H), 7.9 (m, 4 H, 4,5,6,7-H). – ^{13}C NMR: δ = 16.3 [d, ^3J (C,P) = 6.0 Hz, C-11], 65.1 [d, ^2J(C,P) = 6.9 Hz, C-10], 71.9 [d, ^1J(C,P) = 106.6 Hz, C-2], 126.6 [d, ^3J(C,P) = 11.6 Hz, C-6], 128.8 [d, ^2J(C,P) = 4.8 Hz, C-7], 132.7 [d, ^1J(C,P) = 134.3 Hz, C-8], 134.9 [d, ^4J(C,P) = 2.4 Hz, C-5], 135.6 [d, ^2J(C,P) = 12.1 Hz, C-9], 136.9 [d, ^3J(C,P) = 12.6 Hz, C-4], 184.1 [d, ^2J(C,P) = 29.8 Hz, C-3]. – ^{31}P NMR: δ = 28.7 (s). – EI MS; *m/z* (%): 278 (28) [M$^+$], 250 (100). – This compound did not give a satisfactory microanalysis.

Structure Determination of **4**: Crystal data: $C_8H_5Br_2O_3P$, M = 339.91, $P2_1/n$, a = 8.0015(12), b = 6.7075(8), c = 19.596(2) Å, V = 1034.6(2) Å^3, Z = 4, $d_{\text{calcd.}}$ = 2.182 Mg/m^3, μ = 7.965 mm^{-1}, T = 173 K. A pale yellow tablet (0.68 × 0.30 × 0.10 mm) was mounted in inert oil. 3709 intensities were measured (2Θ = 6–50°) using Mo-K_α radiation on a Siemens P4 diffractometer. After absorption correction (ψ scans) 1818 were unique (R_{int} = 0.0376) and 1436 used for all calculations (program SHELXL-93). The structure was solved by direct methods and refined anisotropically on F^2. The final $wR(F^2)$ was 0.0896, with conventional $R(F)$ 0.0345, for 128 parameters. Highest peak 1501, deepest hole −648 e/nm^3. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-100398. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: (internat.) +44(1223)336-033; e-mail: deposit@chemcrys.cam.ac.uk].

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