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An alternative reaction of *ortho*-(*N*-benzylidene)aminophenol with chlorophosphites: formation of 2-(2′-alkoxy)-2-oxo-3-phenyl-5,6-benzo-1,4,2-oxazaphosphorinanes

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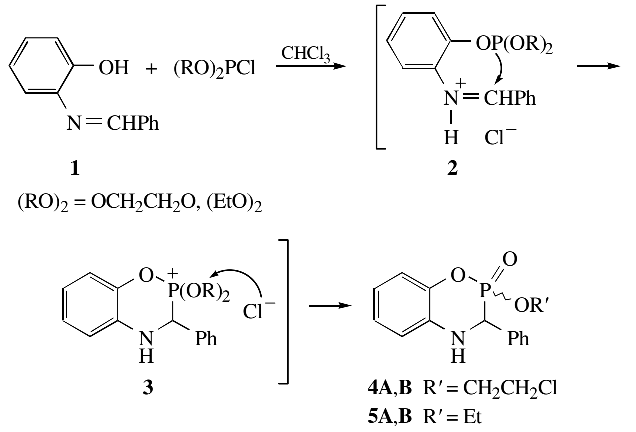
The reactions of *o*-(*N*-benzylidene)aminophenol with ethylene chlorophosphite and diethyl chlorophosphite in $CHCl_3$ in the absence of an external acceptor of HCl result in the formation of diastereomeric 2-(2′-alkoxy)-2-oxo-3-phenyl-5,6-benzo-1,4,2-oxazaphosphorinanes different in the configurations of phosphorus atoms.

The reactions of P^{III} halides with compounds which contain both a hydroxy group and an imino C=N unit have not been widely studied. Several papers describe the formation of polycyclic phosphoranes *via* the reaction of Cl–P^{III} derivatives with phenols containing an imino group in the presence of a base.[1–3] We have observed an alternative reaction pathway in similar systems. Here we report the reactions of *o*-(*N*-benzylidene)aminophenol **1** with ethylene chlorophosphite and diethyl chlorophosphite. These reactions[†] were carried out in the absence of an external HCl acceptor, and they resulted in the formation of two stereoisomers (diastereomers **A** and **B**) of 2-(2′-alkoxy)-2-oxo-3-phenyl-5,6-benzo-1,4,2-oxazaphosphorinanes **4** and **5** differing only in the configuration at the phosphorus atom. The diastereomeric ratio **A**:**B** in both cases was approximately equal to 2:1.



Scheme 1

Diastereomers **4A** and **4B** (from the reaction of imine **1** with ethylene chlorophosphite) and diastereoisomer **5A** (from the reaction of imine **1** with diethyl chlorophosphite) were isolated by column chromatography on silica gel as air-stable colourless crystals. The structures of 2-(2′-chloroethoxy)-2-oxo-3-phenyl-5,6-benzo-1,4,2-oxazaphosphorinane diastereomers **4A** and **4B** were determined by X-ray[‡] diffraction analysis (Figure 1).

The structures of products **5A** and **5B** formed in the reaction of imine **1** with diethyl chlorophosphite were determined by comparing their ^1H NMR and IR spectra with those of diastereomers **4A** and **4B**.[§] In the ^1H NMR spectrum of diastereomer **4A**, the proton of the PCH fragment appears at δ 4.81 ppm, whereas the analogous proton of diastereomer **4B** occurs at a lower field (δ 4.94 ppm). In addition, the magnitude of the geminal coupling $^2J_{HP}$ in **4A** is approximately twice lower than that for diastereomer **4B**.

The ^1H NMR spectrum of a mixture of the two diastereomers of 2-(2′-ethoxy)-2-oxo-3-phenyl-5,6-benzo-1,4,2-oxazaphosphor-

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[†] *A typical experimental procedure was as follows*: A solution of **1** (7.1 mmol) in $CHCl_3$ (5 ml) was added dropwise to a solution of **2** (7.1 mmol) in $CHCl_3$ (10 ml) in a dry argon atmosphere, with cooling (10 °C) and stirring. After stirring for 10 min at this temperature, the reaction mixture was warmed slowly to room temperature and additionally stirred for 2 h; then, it was evaporated to dryness in a vacuum. The residue was purified by column chromatography (silica gel; toluene–acetonitrile, 4:1).

[‡] *X-ray diffraction analysis*. Crystallographic data for **4A** and **4B** at 20 °C: crystals of $C_{15}H_{15}ClNO_3P$ **4A** are orthorhombic, space group $P2_12_12_1$, a = 8.857(6) Å, b = 10.532(2) Å, c = 16.40(1) Å, V = 1529.5(1) Å^3, Z = 4, M = 323.72, d_{calc} = 1.41 g cm^{-3}, μ(CuKα) = 3.327 cm^{-1}, F(000) = 672; crystals of $C_{15}H_{15}ClNO_3P$ **4B** are monoclinic, space group $P2_1/c$, a = 8.70(2) Å, b = 16.698(6) Å, c = 10.942(6) Å, β = 102.10(5)°, V = 1554.8(4) Å^3, Z = 4, M = 323.72, d_{calc} = 1.38 g cm^{-3}, μ(CuKα) = 3.273 cm^{-1}, F(000) = 672. Intensities of 1816 reflections for M10 and 2377 reflections for M11 were measured on an Enraf Nonius CAD-4 diffractometer at 20 °C (λ CuKa radiation, $\omega/2\theta$ scan technique, $2\theta_{max}$ < 144° for M10 and 114° for M11), of which 1710 and 2068 were with $I > 3\sigma$ for M10 and M11, respectively.

The structures were solved by direct methods and difference Fourier syntheses using the SIR program[4] and the MolEN package.[5] All non-hydrogen atoms were refined anisotropically; H atoms located in ΔF maps were refined isotropically. The absolute crystal structure and the absolute configuration of a molecule of **4A** were determined by the Hamilton test ratio[6] with a probability of 95%. The final agreement factors are R 0.034, R_w 0.044 based on 1643 reflections with $F^2 \geq 3\sigma$ for **4A** and R 0.034, R_w 0.046 based on 1955 reflections with $F^2 \geq 3\sigma$ for **4B**. Atomic coordinates, bond lengths, bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). For details, see ‘Notice to Authors’, *Mendeleev Commun.*, Issue 1, 2001. Any request to the CCDC for data should quote the full literature citation and the reference number 1135/96.

[§] ^1H and ^{31}P NMR spectra (solvent: CD_3CN) were measured on Bruker WM-250 (^1H, 250 MHz, TMS) and Bruker MSL-400 (^{31}P, 162 MHz, 85% H_3PO_4) instruments. IR spectra were recorded on a UR-20 spectrometer.

Compound **4**. Overall yield of diastereomers **4A** + **4B** is 73%.

Diastereomer **4A**: mp 149–150 °C. ^1H NMR, δ: 3.51 (m, 2H, CH_2Cl), 3.91 (m, 1H, OCH), 4.08 (m, 1H, OCH′), 4.81 (d, 1H, CHP, ^2J 10.6 Hz), 6.80–7.04 (m, 4H, C_6H_4), 7.44–7.60 (m, 5H, Ph). ^{31}P NMR, δ: 10.6. IR (vaseline oil, KBr, ν/cm^{-1}): 1030, 1043 (P–O–C), 1222, 1252 (P=O), 3275 (N–H). Found (%): C, 55.74; H, 4.68; Cl, 10.48; N, 4.38; P, 9.31. Calc. for $C_{15}H_{15}ClNO_3P$ (%): C, 55.64; H, 4.64; Cl, 10.97; N, 4.33; P, 9.58.

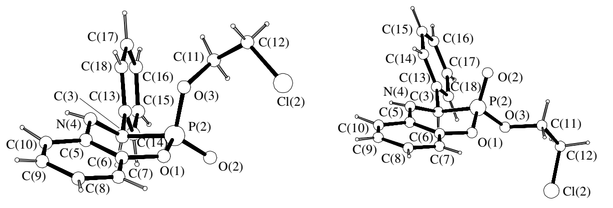
Diastereomer **4B**: mp 90–91 °C. ^1H NMR, δ: 3.76 (m, 2H, CH_2Cl), 4.37 (m, 2H, OCH_2), 4.94 (d, 1H, CHP, ^2J 20.4 Hz), 6.76–7.05 (m, 4H, C_6H_4), 7.39 (m, 5H, Ph). ^{31}P NMR, δ: 11.2. IR (vaseline oil, KBr, ν/cm^{-1}): 1038, 1088 (P–O–C), 1230, 1250 (P=O), 3253 (N–H). Found (%): C, 55.85; H, 4.41; Cl, 11.21; N, 4.19; P, 9.12. Calc. for $C_{15}H_{15}ClNO_3P$ (%): C, 55.64; H, 4.64; Cl, 10.97; N, 4.33; P, 9.58.

Compound **5**. Overall yield of diastereomers **5A** + **5B** is 79%.

Diastereomer **5A**: mp 138–139 °C. ^1H NMR, δ: 1.08 (t, 3H, Me, ^3J 7.5 Hz), 3.83 (m, 1H, OCH), 3.97 (m, 1H, OCH′), 4.78 (d, 1H, CHP, ^2J 11.4 Hz), 6.81–7.03 (m, 4H, C_6H_4); 7.39–7.62 (m, 5H, Ph). ^{31}P NMR, δ: 10.3. IR (vaseline oil, KBr, ν/cm^{-1}): 1035 (P–O–C), 1205, 1260 (P=O), 3292 (N–H). Found (%): C, 62.44; H, 5.60; N, 4.78; P, 10.68. Calc. for $C_{15}H_{16}NO_3P$ (%): C, 62.28; H, 5.54; N, 4.84; P, 10.78.

Mixture of diastereomers **5A** + **5B**, 1:1.3. Light-brown oil, n_D^{20} 1.5670. IR (KBr, ν/cm^{-1}): 1025, 1035, 1070 (P–O–C), 1210, 1223, 1260 (P=O), 3280, 3292 (N–H). Found (%): C, 62.02; H 5.16; N 4.19; P 9.12.

Diastereomer **5B**: ^1H NMR, δ: 1.26 (t, 3H, Me, ^3J 7.1 Hz), 4.23 (m, 2H, OCH_2), 4.87 (d, 1H, CHP, ^2J 19.5 Hz), 6.75–7.07 (m, 4H, C_6H_4), 7.27–7.78 (m, 5H, Ph). ^{31}P NMR, δ: 12.0.



4A **4B**

Figure 1 Molecular structure of diastereomers **A**,**B** of compound **4**. For **4A**, selected bond lengths (Å) : P(2)–O(1) 1.569(2), P(2)–O(2) 1.466(2), P(2)–O(3) 1.572(2), P(2)–C(3) 1.815(2), N(4)–C(3) 1.450(3), N(4)–C(5) 1.394(3), O(1)–C(6) 1.407(3), C(5)–C(6) 1.402(3), C(3)–C(13) 1.511(3); selected bond angles (°): O(1)–P(2)–O(2) 113.0(1), O(1)–P(2)–O(3) 101.8(1), O(1)–P(2)–C(3) 103.0(1), O(2)–P(2)–O(3) 114.9(1), O(2)–P(2)–C(3) 115.5(1), O(3)–P(2)–C(3) 107.0(1), P(2)–O(1)–C(6) 124.5(2), P(2)–O(3)–C(11) 122.9(2), C(3)–N(4)–C(5) 117.6(2), P(2)–C(3)–N(4) 107.1(2), P(2)–C(3)–C(13) 110.4(2), N(4)–C(3)–C(13) 113.6(2), N(4)–C(5)–C(6) 121.1(2), O(1)–C(6)–C(5) 121.2(2), O(1)–C(6)–C(7) 116.8(2). For **4B**, selected bond lengths (Å): P(2)–O(1) 1.584(1), P(2)–O(2) 1.459(2), P(2)–O(3) 1.559(1), P(2)–C(3) 1.810(2), N(4)–C(3) 1.457(2), N(4)–C(5) 1.386(2), O(1)–C(6) 1.413(2), C(5)–C(6) 1.390(2), C(3)–C(13) 1.509(2); selected bond angles (°): O(1)–P(2)–O(2) 113.39(8), O(1)–P(2)–O(3) 102.83(7), O(1)–P(2)–C(3) 102.76(8), O(2)–P(2)–O(3) 115.74(7), O(2)–P(2)–C(3) 116.68(8), O(3)–P(2)–C(3) 103.65(8), P(2)–O(1)–C(6) 120.5(1), P(2)–O(3)–C(11) 121.6(1), C(3)–N(4)–C(5) 122.2(1), P(2)–C(3)–N(4) 105.9(1), P(2)–C(3)–C(13) 111.8(1), N(4)–C(3)–C(13) 111.7(1), N(4)–C(5)–C(6) 122.7(1), O(1)–C(6)–C(5) 120.7(1), O(1)–C(6)–C(7) 116.9(2).

inane **5** formed in the reaction of imine **1** with diethyl chlorophosphite shows two doublets at δ 4.76 (*J* 11.4 Hz) and 4.87 ppm (*J* 19.5 Hz). The ^{1}H NMR spectrum of the isolated product **5A** exhibits a doublet at δ 4.78 ppm (*J* 11.4 Hz). Based on this observation and the earlier result for diastereomers **4A** and **4B**, we can conclude that the isolated diastereomer of **5** has the structure of **5A**, which is analogous to diastereomer **4A**, *i.e.*, the alkoxy group in both cases adopts an axial orientation. The IR spectra of diastereomers **4A**, **4B**, **5A** and **5B** are similar with the most characteristic absorption band for the secondary amino group NH at 3250–3280 $\mathrm{cm^{-1}}$.

The formation of 1,4,2-oxazaphosphorinanes **4** and **5** in the course of the reaction of **1** with chlorophosphites can be illustrated by Scheme 1. Initially formed iminium salts **2** undergo intramolecular cyclization by the nucleophilic attack of the $\mathrm{P^{III}}$ atom at the electrophilic carbon atom of the imonium group, resulting in the formation of quasiphosphonium salts **3**. The latter give final products **4** and **5** according to the second stage of the Arbuzov reaction.

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