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A new direction in the reaction of α-iminocarboxylate salts with dialkyl chlorophosphites: formation of bis[1-(dialkoxyphosphoryl)alkyl]amines

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Sodium benzylidene-L-phenylglycinate and sodium benzylidene-D-alaninate react with dialkyl chlorophosphites and water contained in their crystal lattices to give stereoisomeric bis[1-(dialkoxyphosphoryl)alkyl]amines.

The addition of dialkyl phosphites or their salts to imines is a common method for the synthesis of α-aminophosphonates (including stereoselective synthesis). This phosphorylation of imines derived from α-amino acids (α-imino acids) occurs only with *tert*-butyl *R*-(–)-phenylglycinate derivatives.[1] Recently, α-imino acids were phosphorylated through the carboxylate function using sodium benzylideneglycinate and monochlorophosphites as an example. The reaction resulted in 1,4-bis-[1-(dialkoxyphosphoryl)benzyl]-2,5-diketopiperazines.[2] In this connection, it is of considerable interest to study the stereochemistry of the chiral carbon atom with a P–C bond formed in the reaction and to use this reaction as an approach to the synthesis of chiral α-aminophosphonates, precursors of enantiomerically pure α-aminophosphonic acids. This possibility was

previously shown in the reaction of chiral β-iminoalcohols with dialkyl chlorophosphites.[3,4]

We obtained sodium benzylidene-L-phenylglycinate **1a** and sodium benzylidene-D-alaninate **1b** from L-(+)-phenylglycine and D-(+)-alanine,† respectively, in order to use them as the derivatives of chiral α-iminocarboxylic acids.

Imines **1a**,**b** were unexpectedly found to react quantitatively with dialkyl chlorophosphites in a 1:2 ratio to give stereoisomeric bis[1-(dialkoxyphosphoryl)alkyl]amines **9a–c** as the final products (Scheme 1).‡ Compounds **9a–c** were purified by column chromatography; the analytically pure samples of individual diastereomers were isolated from corresponding eluted fractions. The structures of compounds **9a–c** were proved by NMR spectroscopy (^{1}H, ^{13}C, ^{31}P), mass spectrometry, IR spectroscopy and polarimetry; the compositions were confirmed by elemental analysis.§

† *Sodium benzylidene-L-phenylglycinate* **1a**. L-(+)-Phenylglycine (1.89 g, 13 mmol) was added to a solution of sodium hydroxide (0.52 g, 13 mmol) in 15 ml of anhydrous MeOH. Once the acid had dissolved completely (20 °C), benzaldehyde (1.5 g, 14 mmol) was added with stirring. The suspension formed in the reaction mixture for a day was filtered off; the solvent was removed from the filtrate by evaporation *in vacuo*. The residue was recrystallised from ethanol. Compound **1a** (2.8 g, yield 82%) was obtained as a white powder, mp 235–238 °C (decomp.), $[\alpha]_D^{20}$ +32.5° (*c* 0.88, MeOH). ^{1}H NMR (400 MHz, CD_3OD, TMS), δ: 5.04 [s, 1H, HCC(O)], 7.14–7.95 (m, 10H, 2Ph), 8.36 (s, 1H, HC=N). IR (Vaseline oil, ν/cm^{-1}): 1608 (C=N), 1646 (C=O). Found (%): C, 69.43; H, 5.03; N, 5.38. Calc. for $C_{15}H_{12}NO_2Na$ (%): C, 68.96; H, 4.60; N, 5.36.

Sodium benzylidene-D-alanilate **1b** was obtained similarly to compound **1a** (recrystallisation from Pr^{i}OH). Yield 75%, mp 203–206 °C (decomp.), $[\alpha]_D^{20}$ –13.6° (*c* 1.45, MeOH). ^{1}H NMR (400 MHz, CD_3OD, TMS), δ: 1.47 (d, 3H, Me, $^3J_{HH}$ 7 Hz), 3.99 [q, 1H, CHC(O), $^3J_{HH}$ 7 Hz], 7.40–7.80 (m, 5H, Ph), 8.31 (s, 1H, HC=N). IR (Vaseline oil, ν/cm^{-1}): 1596 (C=N), 1642 (C=O). Found (%): C, 60.63; H, 4.83; N, 7.39. Calc. for $C_{10}H_{10}NO_2Na$ (%): C, 60.30; H, 5.02; N, 7.04.

‡ *Bis[1-(diethoxyphosphoryl)benzyl]amine* **9a**. Diethyl chlorophosphite (1.2 g, 7.7 mmol) in $CHCl_3$ (5 ml) was added with stirring at room temperature under dry argon to a suspension of compound **1a** (1 g, 3.8 mmol) in 10 ml of anhydrous $CHCl_3$. After a day, the precipitate was filtered off; the solvent was removed from the filtrate by evaporation *in vacuo*. Compound **10** (0.5 g) was isolated from the residue by treatment with diethyl ether. The solvent was removed from the ethereal layer by evaporation *in vacuo*, and the residue was chromatographed on Chemapol silica gel (L 100/160 mesh) in the toluene–ethyl acetate system (1:2). The composition of the eluate fractions was monitored by TLC on Silufol UV 254 plates using iodine vapour to visualise the chromatograms. The following compounds were isolated in sequence: **8a** (0.1 g) obtained as a yellowish liquid; 0.09 g of compound **3** (R = Et); **9a** (*meso*) and **9b** (*d*,*l*) obtained as colourless oily liquids. The overall yield of compound **9a** was 1.1 g (61%).

Compounds **9b**,**c** were obtained (similarly to compound **9a**) as colourless oils. Compounds **9b** and **9c** were chromatographed using benzene–acetonitrile (2:1) and toluene–acetonitrile (2:1) as the eluents, respectively. The overall yields are: 55% for **9b** and 67% for **9c**.

§ **9a** (*d*,*l*): n_D^{20} 1.5118, $[\alpha]_D^{20}$ +24.5° (*c* 0.5, AcOEt). ^{1}H NMR (600 MHz, CD_3CN) δ: 1.10, 1.26 (2t, 12H, 4Me, $^3J_{HH}$ 7.1 Hz), 3.76 (d, 2H, 2HCP, $^2J_{HP}$ 21.7 Hz), 3.81, 3.91 (2m, 4H, 2CH_2), 4.03–4.06 (m, 4H, 2CH_2), 7.28–7.38 (m, 10H, 2Ph). ^{13}C-{^{1}H} NMR (150.9 MHz, CD_3CN) δ: 16.52, 16.54, 16.71, 16.73 (4d, 4Me, $^3J_{CP}$ 3.0, 3.1, 3.0, 2.5 Hz), 58.25 (dd, CHP, $^1J_{CP}$ 154.1 Hz, $^3J_{CP}$ 17.6 Hz), 63.73, 63.75, 63.84, 63.86 (4d, 4CH_2, $^2J_{CP}$ 3.6, 4.0, 3.5, 3.5 Hz), 129.16, 129.17 (2d, C^p_{Ph}, $^5J_{CP}$ 1.5 Hz), 129.45, 129.46 (2d, C^m_{Ph}, $^4J_{CP}$ 1.0 Hz), 129.83, 129.85 (2d, C^o_{Ph}, $^3J_{CP}$ 3.0 Hz), 135.56, 135.57 (2d, C^i_{Ph}, $^2J_{CP}$ 2.0, 2.5 Hz). ^{31}P NMR (36.5 MHz, CD_3CN) δ: 21.9 (s). IR (thin layer, ν/cm^{-1}): 1025, 1052 (P–O–C), 1216, 1249 (P=O), 3328 (NH). MS (EI, 70 eV), *m*/*z* (%): 332 (92.0) $[M – P(O)(OEt)_2]^+$, 242 (53.0) $[M – P(O)(OEt)_2 – 2(OEt)]^+$.

9a (*meso*): n_D^{20} 1.5180, $[\alpha]_D^{20}$ 0° (*c* 1.2, AcOEt). ^{1}H NMR (400 MHz, CD_3CN) δ: 1.14, 1.25 (2t, 12H, 4Me, $^3J_{HH}$ 7.1 Hz), 3.88–3.95 (2m, 4H, 2CH_2), 4.05 (m, 4H, 2CH_2), 4.24 (d, 2H, 2HCP, $^2J_{HP}$ 17.3 Hz), 7.28 (m, 10H, 2Ph). ^{13}C-{^{1}H} NMR (150.9 MHz, CD_3CN) δ: 16.53, 16.67 (2d, 4Me, $^3J_{CP}$ 5.5, 5.7 Hz), 59.94 (dd, CHP, $^1J_{CP}$ 151.5 Hz, $^3J_{CP}$ 10.4 Hz), 63.43, 63.63 (2d, 4CH_2, $^2J_{CP}$ 6.8, 7.2 Hz), 128.67 (d, C^p_{Ph}, $^5J_{CP}$ 3.1 Hz), 129.06 (s, C^m_{Ph}), 129.51 (d, C^o_{Ph}, $^3J_{CP}$ 5.3 Hz), 137.57 (m, C^i_{Ph}, $^2J_{CP}$ 2.3 Hz). ^{31}P NMR (CD_3CN) δ: 22.3 (s). IR (thin layer, ν/cm^{-1}): 1024, 1040 (P–O–C), 1216, 1238 (P=O), 3342 (NH).

Compounds **9a**,**b** incorporating two chiral carbon atoms in the same chemical environment are formed as mixtures of *d*,*l* (*RR*+*SS*) and *meso* (*RS*+*SR*) forms. The diastereomers in which the proton of the PCH fragment in the ^{1}H NMR spectrum displays a signal in a lower field and with smaller absolute magnitudes of $^2J_{HP}$ show zero optical rotation ($[\alpha]_D^{20}$ = 0°) (*meso* forms). On the other hand, the diastereomers with an upfield proton of the same fragment and with higher magnitudes of $^2J_{HP}$ show considerable optical rotation angles $[\alpha]_D^{20}$. This allows us to assign them a *d*,*l*-structure with the predominance of one of the enantiomers. The *d*,*l*:*meso* ratios for the raw reaction mixtures are 2.4:1 (**9a**) and 2.1:1 (**9b**). The two

Elemental analysis of a mixture of **9a** (*d*,*l*) and **9a** (*meso*), 1:1. Found (%): C, 56.88; H, 6.82; N, 3.00; P, 12.74. Calc. for $C_{22}H_{33}NO_6P_2$ (%): C, 56.29; H, 7.04; N, 2.98; P, 13.22.

9b (*d*,*l*): n_D^{20} 1.5120, $[\alpha]_D^{20}$ –12.0° (*c* 2.9, C_6H_6). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.00, 1.19, 1.26, 1.27 (4d, 24H, 8Me, $^3J_{HH}$ 6.2 Hz), 2.45 (br. s, 1H, NH), 3.64 (d, 2H, 2HCP, $^2J_{HP}$ 22.0 Hz), 4.41, 4.64 (2m, 4H, 4HCO), 7.27, 7.35–7.36 (2m, 10H, 2Ph). ^{13}C-{^{1}H} NMR (100.6 MHz, CD_3CN) δ: 23.88, 23.90, 24.33, 24.35 (4d, 4Me, $^3J_{CP}$ 2.4, 2.7, 2.4, 2.7 Hz), 24.45, 24.47 (2d, 4Me, $^3J_{CP}$ 0.8–1.0 Hz), 58.68 (dd, CHP, $^1J_{CP}$ 156.0 Hz, $^3J_{CP}$ 17.4 Hz), 72.29, 72.33, 72.42, 72.46 (4d, 4CHO, $^2J_{CP}$ 3.7, 3.6, 3.6, 3.5 Hz), 129.10 (s, C^p_{Ph}), 129.37 (s, C^m_{Ph}), 130.23 (s, C^o_{Ph}), 136.10 (s, C^i_{Ph}). ^{31}P NMR (CD_3CN) δ: 21.6 (*s*). IR (thin layer, ν/cm^{-1}): 990 (P–O–C), 1246 (P=O), 3325 (NH). MS (CI), *m*/*z* (%): 526 (100) $[M + H]^+$.

9b (*meso*): n_D^{20} 1.5165, $[\alpha]_D^{20}$ 0° (*c* 2.5, C_6H_6). ^{1}H NMR (400 MHz, CD_3CN) δ: 1.04, 1.22, 1.25, 1.26 (4d, 24H, 8Me, $^3J_{HH}$ 6.1–6.2 Hz), 4.16 (d, 2H, 2HCP, $^2J_{HP}$ 17.2 Hz), 4.47, 4.60 (2m, 4H, 4CHO), 7.27 (m, 10H, 2Ph). ^{13}C-{^{1}H} NMR (100.6 MHz, CD_3CN) δ: 23.98, 24.23, 24.29, 24.42 (4d, 8Me, $^3J_{CP}$ 5.5, 3.4, 3.3, 5.0 Hz), 60.53 (dd, CHP, $^1J_{CP}$ 151.9 Hz, $^3J_{CP}$ 10.4 Hz), 72.17, 72.52 (2d, 4CHO, $^2J_{CP}$ 7.5, 7.3 Hz), 128.74 (d, C^p_{Ph}, $^5J_{CP}$ 2.8 Hz), 129.10 (br. s, C^m_{Ph}), 129.90 (d, C^o_{Ph}, $^3J_{CP}$ 6.1 Hz), 137.81 (d, C^i_{Ph}, $^2J_{CP}$ 3.4 Hz). ^{31}P NMR (CD_3CN) δ: 22.1 (s). IR (thin layer, ν/cm^{-1}): 991 (P–O–C), 1243 (P=O), 3345 (NH).

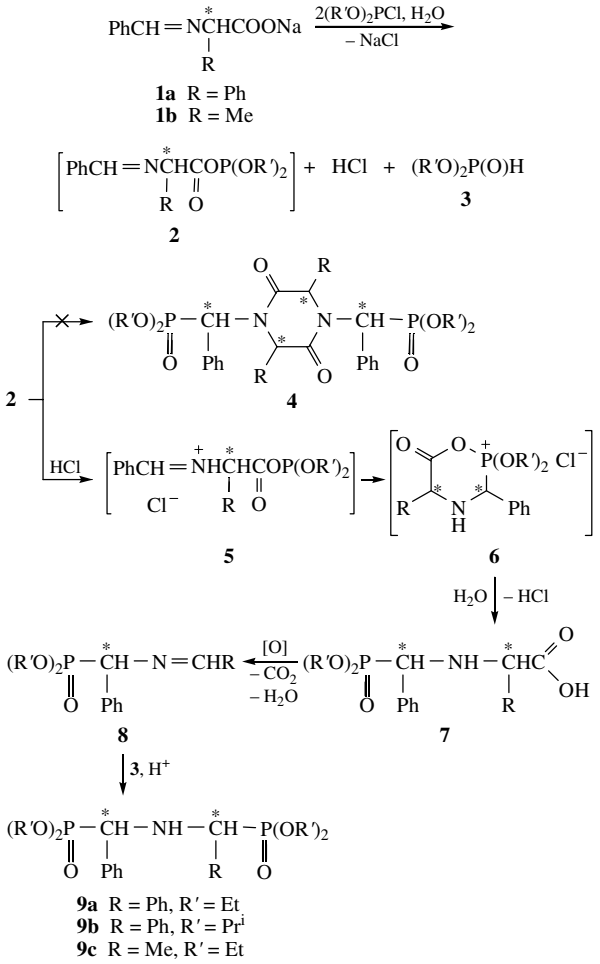
Elemental analysis of a mixture of **9b** (*d*,*l*) and **9b** (*meso*), 1:1. Found (%): C, 56.88; H, 6.82; N, 3.00; P, 12.74. Calc. for $C_{26}H_{41}NO_6P_2$ (%): C, 59.43; H, 7.81; N, 2.67; P, 11.81.

9c (diastereomer d_1): n_D^{20} 1.4880, $[\alpha]_D^{20}$ +6.80° (*c* 1.4, C_6H_6). ^{1}H NMR [600 MHz, $(CD_3)_2CO$)] δ: 1.11, 1.27 (2t, 6H, 2$MeCOP_1$, $^3J_{HH}$ 7.1 Hz), 1.22 (dd, 3H, $MeCP_2$, $^3J_{HH}$ 6.9 Hz, $^3J_{HP}$ 17.5 Hz), 1.27, 1.28 (2t, 6H, 2$MeCOP_2$, $^3J_{HH}$ 7.1 Hz), 2.83 (ddq, 1H, HCP_2, $^2J_{HP}$ 15.2 Hz, $^3J_{HH}$ 7.0 Hz, $^4J_{HP}$ 0.5 Hz), 2.87 (br. s, 1H, NH), 3.37, 3.82 (2m, 2H, H_2COP_1), 4.08–4.10 (m, 6H, H_2COP_1 + 2H_2COP_2), 4.34 (d, 1H, HCP_1, $^2J_{HP}$ 20.3 Hz), 7.32–7.49 (m, 5H, Ph). ^{13}C-{^{1}H} NMR (100.6 MHz, $CDCl_3$) δ: 13.76 (d, *Me*CP_2, $^2J_{CP}$ 1.5 Hz), 16.30 (d, *Me*COP_2, $^3J_{CP}$ 5.8 Hz), 16.44 (d, *C*′H_3COP_2, $^3J_{CP}$ 5.7 Hz), 16.48 (d, *Me*COP_1, $^3J_{CP}$ 5.6 Hz), 16.51 (d, *C*′H_3COP_1, $^3J_{CP}$ 5.8 Hz), 47.28 (dd, CHP_2, $^1J_{CP}$ 159.2 Hz, $^3J_{CP}$ 15.3 Hz), 57.90 (dd, CHP_1, $^1J_{CP}$ 153.8 Hz, $^3J_{CP}$ 15.6 Hz), 62.30 (d, CH_2OP_1, $^2J_{CP}$ 6.7 Hz), 62.45 (d, C′H_2OP_1, $^2J_{CP}$ 7.0 Hz), 63.00 (d, CH_2OP_2, $^2J_{CP}$ 6.9 Hz), 63.05 (d, C′H_2OP_2, $^2J_{CP}$ 7.0 Hz), 128.12 (d, C^p_{Ph}, $^5J_{CP}$ 3.1 Hz), 128.52 (d, C^m_{Ph}, $^4J_{CP}$ 2.4 Hz), 128.85 (d, C^o_{Ph}, $^3J_{CP}$ 6.1 Hz), 135.03 (d, C^i_{Ph}, $^2J_{CP}$ 4.6 Hz). ^{31}P NMR ($CDCl_3$) δ: 23.4 (d, P_1, $^4J_{PP}$ 6 Hz), 28.0 (d, P_2, $^4J_{PP}$ 6 Hz). IR (thin layer, ν/cm^{-1}): 1025, 1050 (P–O–C), 1240 (P=O), 3325 (NH). MS (CI), *m*/*z* (%): 408 (100) $[M + H]^+$. MS (EI, 70 eV), *m*/*z* (%): 270 (70.0) $[M – P(O)(OEt)_2]^+$, 242 (38.0) $[M – P(O)(OEt)_2 – C_2H_4]^+$, 133 (52.0) $[M – P(O)(OEt)_2 – P(O)(OEt)_2]^+$, 132 (100) $[M – P(O)(OEt)_2 – P(O)(OEt)_2 – H]^+$.

9c (diastereomer d_2): n_D^{20} 1.4975, $[\alpha]_D^{20}$ +16.60° (*c* 3.5, C_6H_6). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.10, 1.34 (2t, 6H, 2$MeCOP_1$, $^3J_{HH}$ 7.1 Hz), 1.22 (dd, 3H, $MeCP_2$, $^3J_{HH}$ 7.2 Hz, $^3J_{HP}$ 17.1 Hz), 1.28, 1.29 (2t, 6H, 2$MeCOP_2$, $^3J_{HH}$ 7.1 Hz), 2.81 (dq, 1H, HCP_2, $^2J_{HP}$ 7.2 Hz, $^3J_{HH}$ 7.2 Hz), 3.10 (br. s, 1H, NH), 3.75, 3.92 (2m, 2H, H_2COP_1), 4.08–4.11 (m, 4H, 2H_2COP_2), 4.17 (m, 2H, H_2COP_1), 4.62 (dd, 1H, HCP_1, $^2J_{HP}$ 20.6 Hz, $^4J_{PP}$ 2.0 Hz), 7.28–7.44 (m, 5H, Ph). ^{13}C-{^{1}H} NMR (100.6 MHz, $CDCl_3$) δ: 16.25 (d, *Me*COP_1, $^3J_{CP}$ 5.8 Hz), 16.44 (d, *C*′H_3COP_1, $^3J_{CP}$ 6.0 Hz), 16.63 (d, *Me*COP_2, $^3J_{CP}$ 5.6 Hz), 16.69 (d, *C*′H_3COP_2, $^3J_{CP}$ 5.5 Hz), 17.05 (br. s, *Me*CP_2), 47.81 (dd, CHP_2, $^1J_{CP}$ 155.7 Hz, $^3J_{CP}$ 7.2 Hz), 59.26 (dd, CHP_1, $^1J_{CP}$ 152.6 Hz, $^3J_{CP}$ 2.7 Hz), 61.85 (d, CH_2OP_1, $^2J_{CP}$ 7.8 Hz), 62.60 (d, C′H_2OP_1, $^2J_{CP}$ 7.0 Hz), 62.95 [d, $(CH_2O)_2P_2$, $^2J_{CP}$ 7.0 Hz)], 128.13 (d, C^p_{Ph}, $^5J_{CP}$ 3.0 Hz), 128.55 (d, C^m_{Ph}, $^4J_{CP}$ 2.4 Hz), 128.84 (d, C^o_{Ph}, $^3J_{CP}$ 6.0 Hz), 135.72 (d, C^i_{Ph}, $^2J_{CP}$ 4.4 Hz). ^{31}P NMR ($CDCl_3$) δ: 23.1 (s, P_1), 27.8 (s, P_2). IR (thin layer, ν/cm^{-1}): 1027, 1053 (P–O–C), 1238 (P=O), 3389 (NH).

Elemental analysis of a mixture of **9c** (d_1) and **9c** (d_2), 1:1. Found (%): C, 49.60; H, 7.53; N, 3.50; P, 14.76. Calc. for $C_{17}H_{31}NO_6P_2$ (%): C, 50.12; H, 7.62; N, 3.44; P, 15.23.

diastereomers of compound **9c** (d_1, downfield δ_p, and d_2, upfield δ_p) show considerably different $[\alpha]_D^{20}$ values, probably, due to the stereoselectivity of formation of the P–C bonds (d_1:d_2 = 1.4:1 for the reaction mixture).

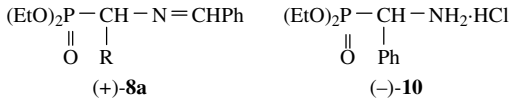


Scheme 1

Most likely, this behaviour of imines **1a**,**b** in reactions with dialkyl chlorophosphites results from the high hygroscopicity of α-iminocarboxylate salts. It is well known that the crystal lattice of such salts can contain several water molecules.[5] Water released during the reaction due to gradual dissolution of imines hydrolyses a fraction of the dialkyl chlorophosphite. The HCl formed reacts with iminoacylphosphites **2** and thus changes the pathway of their subsequent conversions (Scheme 1). No formation of 2,5-diketopiperazines **4** is observed in this case. Immonium salts **5**, similarly to iminoalkylphosphites,[3,4] are converted into phosphorus-containing amino acids **7** through a two-step process involving a heterocyclisation step (intermediate structure **6**), which gives a P–C bond, and a dealkylation step through the Arbuzov reaction followed by the hydrolysis of acyl chlorides formed or by direct hydrolysis of intermediate **6**. The formation of compounds **7** was detected by ^{31}P NMR spectroscopy. In the spectra of raw reaction mixtures, the signals of the phosphorus atoms of compounds **7** are observed at δ 19 ppm. Upon removal of the solvent from the reaction mixtures and treatment of the residues in the presence of atmospheric air, amino acids **7** are oxidised with simultaneous decarboxylation to iminophosphonates **8**. The possibility of such a behaviour of α-amino acids has been reported previously.[6]

The acid-catalysed addition of dialkyl phosphites **3** to imines **8** results in reaction products **9a**–**c**.

The above scheme is in good agreement with the fact that the chromatography of raw reaction products gave the following optically active by-products: iminophosphonate **8a**,¶ its hydrolysis product **10**¶ and dialkyl phosphites **3**.



(+)-**8a** (–)-**10**

Thus, we found a new direction of the reaction of α-iminocarboxylic acids with dialkyl chlorophosphites to give bis-[1-(dialkoxyphosphoryl)alkyl]amines. Taking into account that α-aminophosphonates possess useful properties[7] and display various biological activities,[8] the newly discovered direction is also of practical interest. On the other hand, since the stereocontrolling step of the suggested reaction scheme (**5** → **6**, Scheme 1) probably occurs *via* a six-membered transition state, which is most favourable for attaining a high stereoselectivity, this direction can serve as a basis for the development of the synthesis of optically active α-aminophosphonates.

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¶ **8a**: $[\alpha]_D^{20}$ +7.10° (*c* 8.9, AcOEt). ^{1}H NMR (600 MHz, CD_3CN) δ: 1.19, 1.20 (2t, 6H, 2Me, $^3J_{HP}$ 7.2 Hz), 2.29–2.39 (m, 4H, $2H_2C$), 5.01 (d, 1H, HCP, $^2J_{HP}$ 18.2 Hz), 7.32–7.84 (m, 10H, 2Ph), 8.47 (d, 1H, HC=N, $^4J_{HP}$ 4.8 Hz). ^{13}C NMR (150.9 MHz, CD_3CN) δ: 16.68, 16.73 (2d, 2Me, $^3J_{CP}$ 5.6 Hz), 63.89, 64.07 (2d, $2CH_2$, $^2J_{CP}$ 7.1 Hz), 73.72 (d, CHP, $^1J_{CP}$ 152.1 Hz), 128.61 (d, C^o_{PhCP}, $^5J_{CP}$ 3.1 Hz), 129.18 (d, C^m_{PhCP}, $^4J_{CP}$ 3.3 Hz), 129.19 (s, C^m_{PhCN}), 129.51 (d, C^o_{PhCP}, $^3J_{CP}$ 6.3 Hz), 129.72 (s, C^o_{PhCN}), 132.23 (s, C^p_{PhCN}), 136.97 (d, C^i_{PhCN}, $^4J_{CP}$ 3.1 Hz), 137.77 (d, C^i_{PhCN}, $^2J_{CP}$ 7.6 Hz), 165.49 (d, CH=N, $^3J_{CP}$ 15.8 Hz). ^{31}P NMR (CD_3CN) δ: 19.8 (s). IR (thin layer, ν/cm^{-1}): 1027, 1047 (P–O–C), 1249 (P=O), 1639 (C=N).

10: mp 167–169 °C (from MeOH–MeCN, 2:1), $[\alpha]_D^{20}$ –1.2° (*c* 1.1, MeOH). ^{1}H NMR (600 MHz, CD_3OD) δ: 1.19, 1.29 (2t, 6H, 2Me, $^3J_{HH}$ 7.0 Hz), 3.99, 4.08, 4.11 (3m, 4H, $2H_2CO$), 4.84 (d, 1H, HCP, $^2J_{HP}$ 17.8 Hz), 7.46 (br. m, 3H, $2H^m_{Ph} + 1H^p_{Ph}$), 7.53 (br. d, 2H, $2H^o_{Ph}$, $^3J_{HH}$ 7.1 Hz). ^{13}C-{^{1}H} NMR (150.9 MHz, CD_3OD) δ: 15.40 (d, Me, $^3J_{CP}$ 5.6 Hz), 15.54 (d, CH_3, $^3J_{CP}$ 5.1 Hz), 51.09 (d, CHP, $^1J_{CP}$ 155.1 Hz), 64.77, 64.93 (2d, $2CH_2OP$, $^2J_{CP}$ 7.1 Hz), 128.42 (d, C^o_{Ph}, $^3J_{CP}$ 5.6 Hz), 129.16 (s, C^m_{Ph}), 129.76 (s, C^p_{Ph}), 129.96 (d, C^i_{Ph}, $^2J_{CP}$ 5.6 Hz). ^{31}P NMR (CD_3OD) δ: 17.6 (s).

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