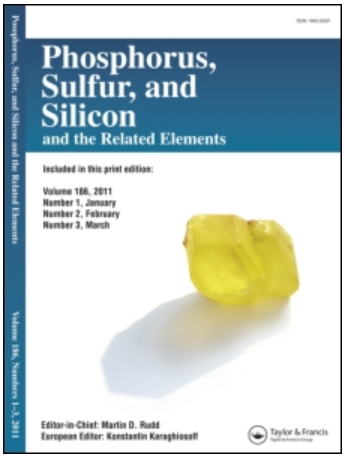

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

SYNTHESIS OF NEW ORGANIC PHOSPHITES CONTAINING STERICALLY HINDERED PIPERIDINE GROUPS

I. Bauer[a]; W. D. Habicher[a]
[a] Institut für Organische Chemie der Technischen Universität Dresden, Dresden, Germany

To cite this Article Bauer, I. and Habicher, W. D.(1997) 'SYNTHESIS OF NEW ORGANIC PHOSPHITES CONTAINING STERICALLY HINDERED PIPERIDINE GROUPS', Phosphorus, Sulfur, and Silicon and the Related Elements, 128: 1, 79 — 103
To link to this Article: DOI: 10.1080/10426509708031565
URL: http://dx.doi.org/10.1080/10426509708031565

Phosphorus, Sulphur, and Silicon, 1997, Vol. 128, pp. 79–103
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SYNTHESIS OF NEW ORGANIC PHOSPHITES CONTAINING STERICALLY HINDERED PIPERIDINE GROUPS

I. BAUER and W. D. HABICHER

Institut für Organische Chemie der Technischen Universität Dresden, Mommsenstr. 13, 01062 Dresden, Germany

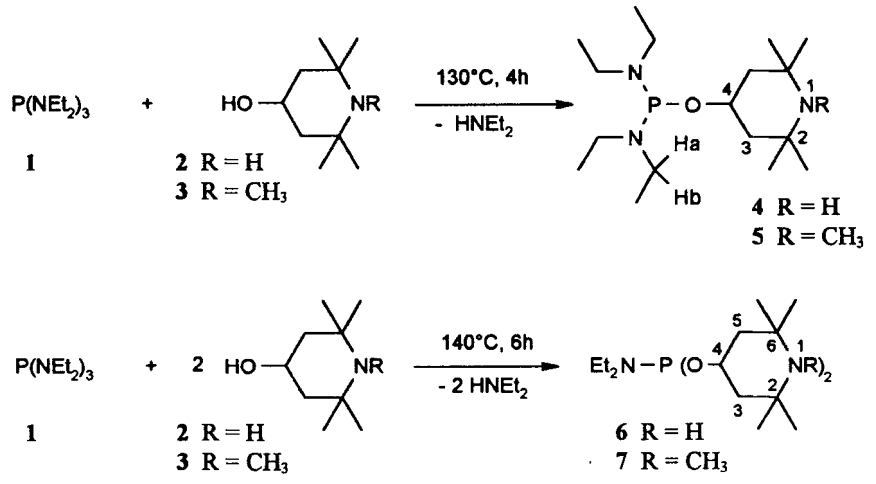
(Received 18 March 1997; In final form 3 June 1997)

The synthesis of several phosphites with sterically hindered piperidine groups which are potential stabilizers for synthetic polymers is described. The reaction of phosphorous acid hexaethyltriamide (**1**) with the 4-hydroxypiperidine compounds **2** and **3** in a 1:1 and 1:2 ratio gives the phosphorous acid monoester diamides **4** and **5** and phosphorous acid diester monoamides **6** and **7**, respectively. These compounds can be selectively hydrolyzed to the phosphorous acid diesters **8** and **9** and to the phosphorous acid monoesters **14** and **15**. The new phosphorous acid ester amides **4**, **5**, **6** and **7** are useful building blocks for the synthesis of phosphites with sterically hindered piperidine moieties. Several representatives of this class of compounds are described.

Keywords: Phosphorous acid ester amides; phosphites; piperidines; ^{31}P NMR, ^{1}H NMR, ^{13}C NMR spectroscopy; synthesis

INTRODUCTION

Organic phosphites are well-known antioxidants for artificial polymers[1,2] whereas hindered amines of the 2,2,6,6-tetramethylpiperidine type are widely used as light stabilizers.[1,3] In commercial applications these types of stabilizers are often used in mixtures with sterically hindered phenols in order to protect the polymer against different damaging influences. We tried to combine these antioxidative active functions in one molecule and synthesized so-called 'HALS-phosphites' (HALS = *H*indered *A*mine *L*ight *S*tabilizer); multifunctional stabilizers[4] whose efficiency as processing,[5] thermo[4–6]—and light stabilizers[4,6,7] was tested and often proved to be better than those of the corresponding mixtures of the individual compounds. This new class of stabilizers excelled in their



SCHEME 1 Reaction of 4-hydroxypiperidines **2** and **3** with $P(NEt_2)_3$ (**1**)

hydrolytic stability[8] which is an important feature for industrial application making these compounds suitable for long term storage.

The compounds synthesized were obtained by reaction of PCl_3 with alcohols or phenols via phosphorous acid monoester dichlorides or cyclic phosphorous acid diester monochlorides.[4,9]

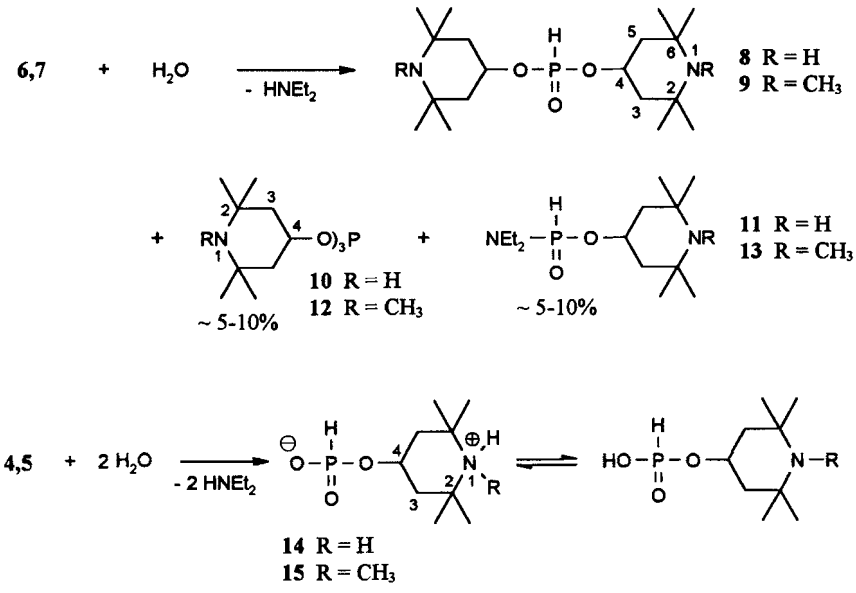
These intermediates were further esterified with 4-hydroxy-2,2,6,6-tetramethylpiperidine compounds to the HALS-phosphites. As this method involves some difficulties (no selective stepwise esterification, hydrochloride formation with the hindered piperidines) we searched for universally applicable HALS-phosphite building-blocks. Herein we report our synthetic work to obtain such building-blocks based on HALS containing phosphorous acid ester amides and their reactions with alcohols, phenols and water.

RESULTS AND DISCUSSION

Synthesis of HALS Containing Phosphorous Acid Ester Amides

The reaction of 4-hydroxy-2,2,6,6-tetramethylpiperidine (**2**) and 4-hydroxy-1,2,2,6,6-pentamethylpiperidine (**3**) with $P(NEt_2)_3$ (**1**) was carried out in 1:1 and 2:1 ratios without solvent (Scheme 1).

For the substitution of one diethylamino group of **1** temperatures between 90–130°C were required for the non-catalyzed reaction whereas substitution of the



SCHEME 2 Hydrolysis of the phosphorous acid ester amides **4**, **5**, **6** and **7**

second diethylamino group proceeded at about 120–140°C. Diethylamine formed was removed in a stream of nitrogen. The phosphorous acid ester amides (**4–7**) were obtained in medium yields and all of them could be purified by distillation *in vacuo*, forming viscous, colorless oils. They are relatively stable towards hydrolysis and oxidation and can be stored unchanged for months.

Hydrolysis Products of Phosphorous Acid Ester Amides

Heating of compounds **6** and **7** with a stoichiometric amount of water leads to hydrolysis and formation of the two phosphorous acid diesters **8** and **9** (Scheme 2).

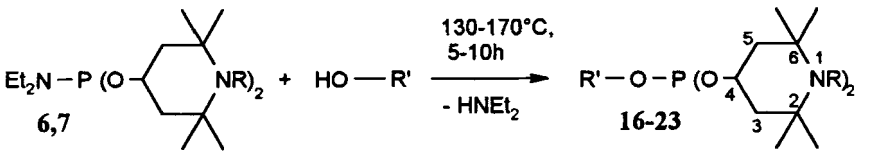
The reaction is straightforward. The ^{31}P NMR spectrum of the crude product of the hydrolysis of **6** showed beside the expected peak at 4.0 ppm for **8** two small peaks for byproducts at 138.2 ppm and 12.2 ppm. The first one belongs to phosphorous acid tris(2,2,6,6-tetramethylpiperidin-4-yl ester) (**10**) which was synthesized independently according to[9] (analytical characterization see experimental section). The second peak (^{31}P NMR: δ = 12.2 (m_cd, $^1J_{PH}$ = 631 Hz)) probably belongs to the corresponding diethyl phosphoramidous acid 2,2,6,6-tetramethyl-piperidin-4-yl ester (**11**). The same result was found for the synthesis of **9**. Small amounts of phosphorous acid tris(1,2,2,6,6-pentamethylpiperidin-4-

yl ester)[9] (**12**) (analytical characterization see experimental section) and diethyl phosphoramidous acid 2,2,6,6-tetramethylpiperidin-4-yl ester (**13**) (^{31}P NMR: δ = 12.6 (m_cd, $^1J_{PH}$ = 643 Hz)) were found. This fact shows that water does not exclusively substitute the diethylamino group from **8** and **9** but to a less extend the hindered piperidine moiety to give the phosphorous acid monoester monoamides. 4-Hydroxypiperidines **1** or **2** released during this process further react with the starting material **6** or **7** to yield the phosphorous acid triesters **10** and **12**, respectively (Scheme 2).

Phosphorous acid diesters formed as main products by the hydrolysis of **6** and **7** were purified by distillation *in vacuo*. In the case of compound **8** it is not possible to separate residues of the starting material **4** by this method because the two compounds have almost the same boiling point at the pressure applied.

Phosphorous acid monoester diamides **4** and **5** were hydrolyzed to give the phosphorous acid monoesters **14** and **15** (Scheme 2). Both compounds exist in an equilibrium between the uncharged form and the betaine structure due to the acidic OH group at the phosphorus and the strong amino base in the piperidine moiety. ^{13}C NMR shifts for the carbon atoms in the 2- and 6-positions on the piperidine ring give a spectroscopic indication for the existence of the betaine structure of **14** and **15**. In comparable uncharged compounds the signals appear at about 51–52 ppm for the phosphorous acid tetramethylpiperidin-4-yl esters (see experimental part, compounds **4**, **6**, **8**, **16–22**, **24**) and 55–56 ppm for the pentamethylpiperidin-4-yl esters (see experimental part, compounds **5**, **7**, **9**, **23**). In the case of phosphorous acid monoesters **14** and **15** these peaks are significantly shifted downfield to 58.9 ppm for **14** and 67.1 ppm for **15**. This is obviously the effect of the positive charge on the nitrogen atom. The typical pattern of signals in the ^{13}C NMR spectrum for the *cis*- and *trans*-methyl groups in the 2- and 6-positions also changes. In phosphorous acid di- and triesters containing 2,2,6,6-tetramethylpiperidinyl groups two singlets at about 34 ppm and 29 ppm are usually observed for the *cis*-Me and *trans*-Me, respectively. In the case of compound **14** the signals of these groups are shifted upfield to 30.6 ppm and 26.6 ppm. In phosphorous acid di- and triesters containing 1,2,2,6,6-pentamethylpiperidinyl groups the *cis*-Me and *trans*-Me groups give two singlets at about 34 ppm and 21 ppm, whereas in compound **15** they appear at 30.6 ppm and 22.3 ppm.

When there is a chiral center in the molecule the methyl groups in the 2- and 6-positions are not magnetically equivalent. This also occurs when two equivalent piperidine moieties are bound to a prochiral phosphorus atom. However, the non-equivalence of the methyl groups in the 2- and 6-positions was not shown by ^{13}C NMR.



SCHEME 3 Reaction of the phosphorous acid ester amides **6** and **7** with alcohols and phenols

The phosphorous acid monoesters **14** and **15** are very stable towards hydrolysis. This is due to an increased electron density at the phosphorus atom. The compounds can be kept unchanged in an aqueous solution at 70°C for many days.

Synthesis of HALS-phosphites

Compounds **6** and **7** were used as starting materials for the synthesis of HALS containing phosphites. They readily react with alcohols and phenols (Scheme 3) without solvent at temperatures of 130–170°C to give the corresponding phosphites which are summarized in Table I.

Because of the relatively low reactivity of the phosphorous acid amides this reaction is limited to non-hindered alcohols and phenols. Reaction of **6** or **7** with 2,6-di-*tert*-butyl-4-methylphenol, for instance, fails due to the bulky substituents in the *ortho* position of the phenol. Only the starting materials are recovered. Very often the HALS-phosphites obtained form hydrates due to their piperidine moieties. This offers a convenient way to isolate them by adding water to their ethanolic or acetonitrile solution. These hydrates are low melting white powders which lose water when stored in a desiccator to give oily products. The pure HALS-phosphites are often viscous oils which sometimes crystallize within months. The structure of compound **23** was confirmed by X-ray analysis.[10] It shows that the oxygen atoms occupy equatorial positions in the piperidine ring. This can also be proved for the other HALS-phosphites by ^{1}H NMR spectroscopy. An example is given in Figure 1 for compound **12** (see also experimental section for the other compounds). *Cis*-3-H can be identified by its strong $^3J_{aa}$-coupling of about 10–12 Hz to the 4-H. As its $^2J_{ae}$-coupling to the *trans*-3-H is also about 12 Hz a doublet of a doublet with the appearance of a triplet is obtained. On the other hand the *trans*-3-H shows a strong coupling with the *cis*-3-H ($^2J_{ae} \sim 12$ Hz) but a weak coupling with the 4-H ($^3J_{ae} \sim 3$–5 Hz) to give a well-separated doublet of a doublet (Figures 1 and 2a, see also experimental section). If the oxygen was in an axial position no strong $^3J_{aa}$-coupling of about 10–12 Hz with 4-H would be possible either for the *cis*-3-H or the *trans*-3-H

TABLE I Reaction conditions, ^{31}P NMR shifts and melting points of HALS-phosphites **16–23**

R'	*R*	*T* [°C]	*t* [h]	$\delta(^{31}P)$ [ppm]	*yield* [%]	*m.p.* [°C]	
16 stearyl	H	160	6	138.5	61	viscous oil **16a**: 31–36	(anhydrous) (hydrate)
17 α-tocopheryl	H	130	6	141.4	97	viscous oil	
18 cholesteryl	H	130	6	138.8	73	52–55 **18a**: 41–42.5	(anhydrous) (ethanol-water-adduct)
19 1(α)-naphthyl-methyl	H	130	8	139.1	40	viscous oil **19a**: 33–35	(anhydrous) (mono-hydrate)
20 1(α)-naphthyl	H	150	6	135.5	29	viscous oil **20a**: 33–38	(anhydrous) (dihydrate)
21 (1-methylethylidene) di-4,1-phenylene	CH_3	150	5	135.8	79	amorphous solid **21a**: 33–36	(anhydrous) (tetra-hydrate)
22 1,4-phenylenebis [(1-methylethylidene)-2,6-dimethyl-4,1-phenylene]	H	150	7	139.3	60	57–65 amorphous solid	
23 1,4-phenylenebis [(1-methylethylidene)-2,6-dimethyl-4,1-phenylene]	CH_3	150	7	139.3	34	177–179	

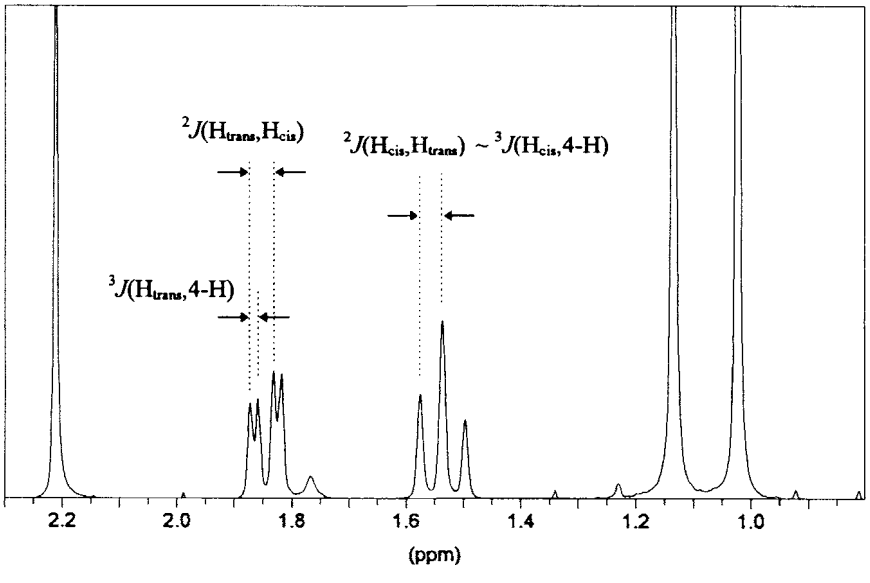


FIGURE 1 Part of the ^1H NMR spectrum of **12**

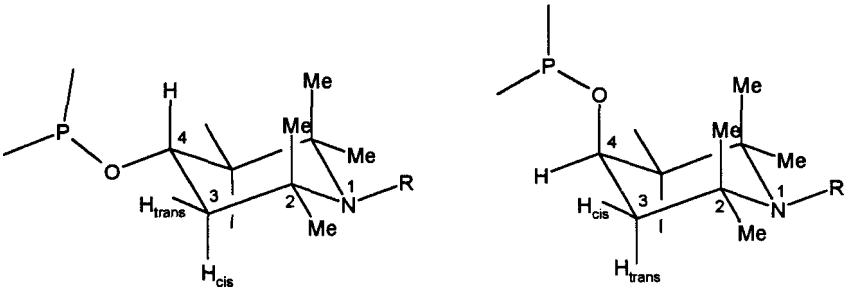


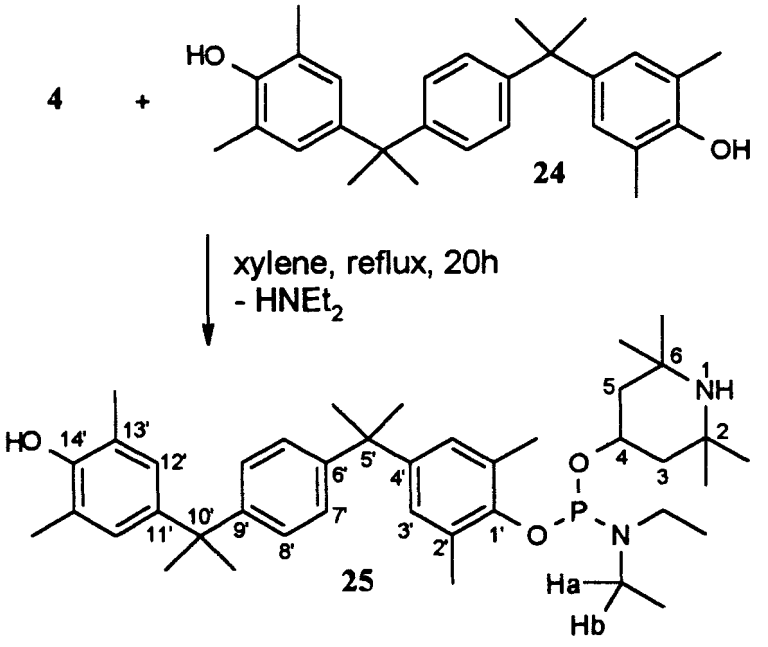
FIGURE 2 Conformation of the piperidine ring in HALS-phosphites

(Figure 2b). These results are in agreement with those of Chen *et al.*[11] who found by means of ^1H NMR spectroscopy that 2,2,6,6-tetramethylpiperidin-4-ol exists predominantly in a chair conformation with the oxygen occupying an equatorial position.

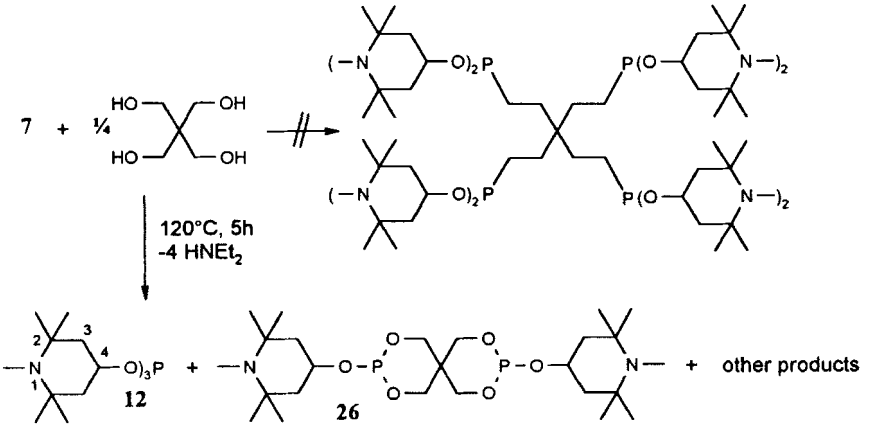
The diethylamino groups of compounds **4** and **5** can be substituted by alkoxy or aryloxy groups by reaction with alcohols and phenols in 1:1 and 1:2 ratios. The ease of substitution depends on how sterically hindered the alcohol or phenol is. The substitution of the second diethylamino function is often very difficult. With sterically hindered phenols only phosphorous acid diester monoamides could be formed.

In the case of the reaction of **4** with bisphenol **24** the monosubstituted product **25** with a free OH group could be isolated (Scheme 4). This compound is especially interesting for application as a polymer stabilizer because it contains three active stabilizing functions in one molecule including the phenolic OH-group.

An attempt to esterify all four OH groups of pentaerythritol with four equivalents of **7** failed. Instead, apart from other byproducts, the main product obtained and isolated was phosphorous acid triester **12** (Scheme 5). The mechanism can be explained as follows. After initial substitution of one OH group of pentaerythritol with **7** the neighboring OH group attacks the phosphorus atom leading to a transesterification reaction resulting in the formation of the spirocompound **26**. One molecule of 4-hydroxypiperidine **3** is released which reacts with the starting material **7** to yield phosphorous acid triester **12**. Half of the starting material **7** can be transformed into the phosphorous acid triester **12**. The rest should form the spirocompound **26** (described in [12]). The ^{31}P NMR peak of this compound ($^{31}P\{^1H\}$ NMR: δ = 123.1 ppm) was found in the product mixture apart from peaks of hydrolysis products. The peak could be



SCHEME 4 Reaction of the phosphorous acid ester amide **4** with bisphenol **24**



SCHEME 5 Reaction of the phosphorous acid ester amide **7** with pentaerythritol

assigned by comparison with the ^{31}P NMR shift for the similar compound 3,9-bis(2,2,6,6-tetramethyl-4-piperidyloxy)-2,4,8,10-tetraoxa-3,9-diphospha-spiro[5.5]undecane described in[4] ($^{31}P\{^1H\}$ NMR: δ = 123.9 ppm).

EXPERIMENTAL

Melting points were determined on a Boëtius melting-point apparatus. ^1H NMR (TMS internal reference), ^{13}C NMR (TMS internal reference) and ^{31}P NMR spectra (85% H_3PO_4 external reference) were recorded either on a Bruker AC-200 P or on a Bruker AC-300 P spectrometer. ^{13}C NMR peaks were assigned by means of DEPT (Distortionless Enhancement by Polarisation Transfer). Assignment of some ^{13}C NMR signals was done by comparison with similar examples from.[13] Atoms in sketches are numbered according to their theoretical magnetic non-equivalence excluding non-equivalence phenomena caused by hindered rotation. Theoretical magnetic non-equivalence is not always resolved in NMR spectra. IR spectra were performed on a Nicolet 250 FT IR spectrometer. Microanalyses were recorded on a CHN-S analyzer (Carlo Erba). Solvents were purified by conventional methods.

4-Hydroxy-2,2,6,6-tetramethylpiperidine **2** and 4-hydroxy-1,2,2,6,6-pentamethylpiperidine **3** were kindly donated by HÜLS AG. Bisphenol **24** was kindly donated by Mitsui Petrochemicals Co.

General procedure for the synthesis of phosphorous acid piperidin-4-yl ester diethylamides 4–7 (GP1)

Phosphorous acid hexaethyltriamide (**1**) was placed in a flame-dried and nitrogen rinsed two-neck flask which was equipped with a gas inlet tube and a micro distillation apparatus. The distillation receiver was cooled with dry ice/acetone. The reported amount of 4-hydroxy-piperidine (**2** or **3**) was added. No solvent is required. The mixture was heated with stirring to the reported temperature. Thereby 4-hydroxypiperidines **2** or **3** dissolved in phosphorous acid triamide **1**. Dietylamine was removed in a stream of nitrogen and collected in a cold trap. The amount of diethylamine trapped could be used to monitor the reaction. For completion of the reaction the mixture was continuously stirred for a certain time at the reported temperature. The products were distilled under reduced pressure.

Tetraethyl phosphorodiamidous acid 2,2,6,6-tetramethyl piperidin-4-yl ester (4)

The reaction was carried out according to the general procedure (GP1) with 40 g (0.16 mol) of phosphorous acid hexaethyltriamide (**1**) and 12.7 g (0.08 mol) of 2,2,6,6-tetramethylpiperidin-4-ol (**2**). The mixture was stirred for 4 h at 130 °C. Excess of **1** was removed by distillation *in vacuo*. Yield: 17.2 g (65%); b.p. 89–92 °C/0.07 torr (colorless oil).

$^{31}P\{^1H\}$ NMR (C_6D_6, 81.1 MHz): δ = 131.6.

^1H NMR (C_6D_6, 200.1 MHz): δ = 4.18 (m_c, 1 H, 4-H), 3.21–2.86 (m, 8 H, $NCH_aH_bCH_3$), 1.95 (dd, J = 4.7, 11.5 Hz, 2 H, *trans*-3-H), 1.21 (dd, J = 11.5, 11.5 Hz, 2 H, *cis*-3-H), 1.11, 1.03 (2 s, 6 H each, *cis*-2-Me, *trans*-2-Me), 1.05 (t, J = 7.1 Hz, 12 H, NCH_2CH_3), 0.32 (s, br., 1 H, NH).

^{13}C NMR (C_6D_6, 50.3 MHz): δ = 68.6 (d, $^2J_{PC}$ = 19.5 Hz, C-4), 51.9 (C-2), 47.6 (d, $^3J_{PC}$ = 4.3 Hz, C-3), 39.8 (d, $^2J_{PC}$ = 19.7 Hz, NCH_2CH_3), 35.8, 30.4 (2 Me each, *trans*-2-Me, *cis*-2-Me), 15.8 (d, $^3J_{PC}$ = 3.0 Hz, NCH_2CH_3).

IR (film): $\tilde{\nu}$ = 3300 cm^{-1} (N-H), 2950 (C-H), 2930 (C-H), 2870 (C-H), 1460 (H-C-H), 1375 (H-C-H), 1237, 1195, 1020 (P-O-C), 908.

$C_{17}H_{38}N_3OP$ (331.5) calcd.: C 61.63 H 11.48 N 12.69

found: C 61.63 H 11.92 N 12.99

Tetraethyl phosphorodiamidous acid 1,2,2,6,6-pentamethyl piperidin-4-yl ester (5)

The reaction was carried out according to the general procedure (GP1) with 61 g (0.25 mol) of phosphorous acid hexaethyltriamide (**1**) and 28.2 g (0.16 mol) of 2,2,6,6-pentamethylpiperidin-4-ol (**3**). The mixture was stirred 4 h at 130 °C. Excess of **1** was removed by distillation *in vacuo*. Yield: 38.7 g (70%); b.p. 115 °C/0.15 torr (colorless oil).

$^{31}P\{^1H\}$ NMR (C_6D_6, 81.1 MHz): δ = 131.5.

^1H NMR (C_6D_6, 200.1 MHz): δ = 4.05 (m_c, 1 H, 4-H), 3.20–2.83 (m, 8 H, $NCH_aH_bCH_3$), 2.15 (s, 3 H, 1-Me), 1.92 (dd, J = 4.1, 12.2 Hz, 2 H, *trans*-3-H), 1.60 (dd, J = 11.6, 11.6 Hz, 2 H, *cis*-3-H), 1.11, 0.96 (2 s, 6 H each, *trans*-2-Me, *cis*-2-Me), 1.04 (t, J = 7.0 Hz, 12 H, NCH_2CH_3).

^{13}C NMR (C_6D_6, 50.3 MHz): δ = 67.2 (d, $^2J_{PC}$ = 19.6 Hz, C-4), 55.8 (C-2), 49.9 (d, $^3J_{PC}$ = 4.3 Hz, C-3), 39.8 (d, $^2J_{PC}$ = 19.7 Hz, NCH_2CH_3), 34.0, 21.5 (*trans*-2-Me, *cis*-2-Me), 28.7 (1-Me), 15.8 (d, $^3J_{PC}$ = 3 Hz, NCH_2CH_3).

IR (film): $\tilde{\nu}$ = 2960 cm^{-1} (C-H), 2932 (C-H), 2864 (C-H), 1458 (H-C-H), 1375 (H-C-H), 1362, 1255, 1195, 1039 (P-O-C), 910, 788, 663.

$C_{18}H_{40}N_3OP$ (345.5) calcd.: C 62.61 H 11.59 N 12.17

found: C 62.66 H 11.89 N 12.86

Diethyl phosphoramidous acid bis(2,2,6,6-tetramethyl piperidin-4-yl ester) (6)

The reaction was carried out following the general procedure (GP1) with 40 g (0.16 mol) of phosphorous acid hexaethyltriamide (**1**) and 50.7 g (0.32 mol) of 2,2,6,6-tetramethylpiperidin-4-ol (**2**). The mixture was stirred for 6 h at 140 °C. Yield: 31.8 g (48%); b.p. 140 °C/0.15 torr (viscous, colorless oil).

$^{31}P\{^1H\}$ NMR (C_6D_6, 81.1 MHz): δ = 144.3.

^1H NMR (C_6D_6, 200.1 MHz): δ = 3.73 (m_c, 2 H, 4-H), 2.63 (dq, J = 7.2 Hz, $^3J_{PH}$ = 7.2 Hz, 4 H, NCH_2CH_3), 1.54 (dd, J = 3.4, 12.6 Hz, 2 H, *trans*-3-or 5-H), 1.43 (dd, J = 2.9, 12.8 Hz, 2 H, *trans*-5-or 3-H), 0.75, 0.69 (2 s, 12 H each, *cis*-2,6-Me, *trans*-2,6-Me), 0.67* (t, J = 7.2 Hz, 6 H, NCH_2CH_3), 0.21 (s, 1 H, NH).* The signal is partly covered by the singlet at 0.69 ppm. Signals for another 4 H (*cis*-3-H and *cis*-5-H) are completely covered by the singlets at 0.75 ppm and 0.69 ppm.

^{13}C NMR (C_6D_6, 50.3 MHz): δ = 66.6 (d, $^2J_{PC}$ = 16.4 Hz, C-4), 51.0 (C-2, C-6), 46.4 (d, $^3J_{PC}$ = 4.0 Hz, C-3, C-5), 37.1 (d, $^2J_{PC}$ = 20.8 Hz, NCH_2CH_3), 34.6, 28.7 (4 Me each, *cis*-2,6-Me, *trans*-2,6-Me), 14.7 (d, $^3J_{PC}$ = 3.3 Hz, NCH_2CH_3).

IR (film): $\tilde{\nu}$ = 3300 cm^{-1} (N-H), 2950 (C-H), 2930 (C-H), 2867 (C-H), 1460 (H-C-H), 1376 (H-C-H), 1365, 1236, 1189, 1020 (P-O-C), 980, 746.

$C_{22}H_{46}N_3O_2P$ (415.6) calcd.: C 63.61 H 11.08 N 10.12

found: C 63.17 H 11.26 N 10.30

Diethyl phosphoramidous acid bis(1,2,2,6,6-pentamethyl piperidin-4-yl ester) (7)

The reaction was carried out according to the general procedure (GP1) with 35.8 g (0.14 mol) of phosphorous acid hexaethyltriamide (**1**) and 49.6 g (0.29 mol) of 1,2,2,6,6-pentamethylpiperidin-4-ol (**3**). The mixture was stirred for 6 h at 140 °C. Yield: 24.2 g (37.6%); b.p. 156 °C/0.05 torr (viscous, colorless oil).

$^{31}P\{^1H\}$ NMR (C_6D_6, 81.1 MHz): δ = 144.1.

^1H NMR (C_6D_6, 200.1 MHz): δ = 4.24 (m_c, 2 H, 4-H), 3.13 (m_c, 4 H, NCH_2CH_3), 2.14 (s, 6 H, 1-Me), 2.10–1.87 (m, 4 H, *trans*-3,5-H), 1.67 (m_c, 4 H, *cis*-3,5-H), 1.11, 0.97 (2s, 12 H each, *cis*-2,6-Me, *trans*-2,6-Me), 1.07* (t, J = 7.1 Hz, 6 H, NCH_2CH_3). *The Signal is partly covered by the singlet at 1.11 ppm.

^{13}C NMR (C_6D_6, 50.3 MHz): δ = 66.6 (d, $^2J_{PC}$ = 15.7 Hz, C-4), 55.7 (C-2, C-6), 50.0 (d, $^3J_{PC}$ = 3.8 Hz, C-3, C-5), 38.5 (d, $^2J_{PC}$ = 20.7 Hz, NCH_2CH_3), 34.0, 21.5 (4 Me each, *cis*-2,6-Me, *trans*-2,6-Me), 28.6 (1-Me), 15.9 (d, $^3J_{PC}$ = 3.4 Hz, NCH_2CH_3).

IR (film): $\tilde{\nu}$ = 2967 cm^{-1} (C-H), 2934 (C-H), 2896 (C-H), 1458 (H-C-H), 1376 (H-C-H), 1362, 1250, 1187, 1025 (P-O-C), 958, 788.

Phosphorous acid bis(2,2,6,6-tetramethyl piperidin-4-yl ester) (8)

11.35 g (27.3 mmol) of phosphorous acid diester monoamide **6** were mixed with 0.49 g (27.3 mmol) of water. The mixture was heated and stirred for 1 h at 150°C. The product was distilled under reduced pressure and crystallized after a couple of weeks.

Yield: 5.6 g (57.1%); b.p. 142 °C/0.05 torr; m.p. 296–297°C.

^{31}P NMR ($CDCl_3$, 121.5 MHz): δ = 4.0 (td, $^3J_{PH}$ = 6.7 Hz, $^1J_{PH}$ = 691.7 Hz)

^1H NMR ($CDCl_3$, 300.1 MHz): δ = 6.78 (d, $^1J_{PH}$ = 693.0 Hz, 1 H, P*H*), 4.69 (m_c, 2 H, 4-H), 1.90 (dd, J = 4.3, 12.5 Hz, 4 H, *trans*-3,5-H), 1.13 (dd, J = 11.6, 11.6 Hz, 4 H, *cis*-3,5-H), 1.06, 1.01 (2 s, 12 H each, *trans*-2,6-Me, *cis*-2,6-Me), 0.65 (s, br., 1 H, N*H*).

^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 71.8 (d, $^2J_{PC}$ = 6.0 Hz, C-4), 51.4 (C-2, C-6), 45.9 (d, $^3J_{PC}$ = 3.7 Hz, C-3 or C-5), 45.7 (d, $^3J_{PC}$ = 4.1 Hz, C-3 or C-5), 34.6, 28.8 (*trans*-2,6-Me, *cis*-2,6-Me).

IR (film): $\tilde{\nu}$ = 3261 cm^{-1} (N-H), 2967 (C-H), 2936 (C-H), 2867 (C-H), 2375 (P-H), 1450 (H-C-H), 1379 (H-C-H), 1368, 1293, 1215, 1053, 1014 (P-O-C), 968, 840.

$C_{18}H_{37}N_2O_3P$ (360.5) calcd.: C 59.97 H 10.35 N 7.77

found: C 60.30 H 10.87 N 7.87

Phosphorous acid bis(1,2,2,6,6-pentamethyl piperidin-4-yl ester) (9)

12.95 g (29.2 mmol) of phosphorous acid diester monoamide **7** were mixed with 0.526 g (29.2 mmol) of water. The mixture was heated and stirred for 1 h at 150°C. The product was distilled under reduced pressure.

Yield: 4.8 g (42.3%); b.p. 167–170 °C/0.15 torr (viscous, colorless oil).

^{31}P NMR (C_6D_6, MHz): δ = 4.6 (td, $^1J_{PH}$ = 686.9 Hz, $^3J_{PH}$ not determined).

^1H NMR (C_6D_6, 200.1 MHz): δ = 6.92 (d, $^1J_{PH}$ = 686.9 Hz, 1 H, P*H*), 4.84 (m_c, 2 H, 4-H), 2.05 (s, 6 H, 1-Me), 2.01-1.90 (m, 4 H, *trans*-3,5-H), 1.69 (dd, J = 11.6, 11.6 Hz, 2 H, *cis*-3 or 5-H), 1.66 (dd, J = 11.6, 11.7 Hz, 2 H, *cis*-3 or 5-H), 1.05 (s, 12 H, *cis*-2,6-Me or *trans*-2,6-Me), 0.90, 0.88 (2 s, 6 H each, *cis*-2 and 6-Me or *trans*-2 and 6-Me).

^{13}C NMR (C_6D_6, 50.3 MHz): δ = 70.9 (d, $^2J_{PC}$ = 5.7 Hz, C-4), 55.7 (C-2, C-6), 49.1 (d, $^3J_{PC}$ = 3.7 Hz, C-3 or C-5), 48.8 (d, $^3J_{PC}$ = 4.4 Hz, C-3 or C-5), 33.7, 21.1 (4 Me each, *cis*-2,6-Me, *trans*-2,6-Me), 28.4 (1-Me).

IR (film): $\tilde{\nu}$ = 2969 cm^{-1} (C-H), 2942 (C-H), 2904, 2874 (C-H), 2432 (P-H), 1459 (H-C-H), 1378 (H-C-H), 1363, 1257, 1186, 1118, 1034 (P-O-C), 975.

Phosphorous acid tris(2,2,6,6-tetramethylpiperidin-4-yl ester) (10)

Compound **10** was synthesized according to.[9] Yield: 42%; m.p. 79–81°C (white powder).

$^{31}P\{^1H\}$ NMR ($CDCl_3$, 81.1 MHz): δ = 139.3.

^1H NMR ($CDCl_3$, 200.1 MHz): δ = 4.46 (m_c, 3 H, 4-H), 1.90 (dd, J = 4.3, 12.7 Hz, 6 H, *trans*-3,5-H), 1.15, 1.09 (2 s, 18 H each, *cis*-2-Me, *trans*-2-Me). The Signals for 6 H (*cis*-3-H) are completely covered by signals at 1.15 ppm and 1.09 ppm.

^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 66.9 (d, $^2J_{PC}$ = 11.1 Hz, C-4), 51.5 (C-2), 46.9 (d, $^3J_{PC}$ = 3.3 Hz, C-3), 34.8, 28.8 (6 Me each, *cis*-2-Me, *trans*-2-Me).

Phosphorous acid tris(1,2,2,6,6-pentamethylpiperidin-4-yl ester) (12)

Synthesis according to.[9] Yield: 77%; m.p. 121–123°C (white powder).

$^{31}P\{^1H\}$ NMR ($CDCl_3$, 81.1 MHz): δ = 138.7.

^1H NMR ($CDCl_3$, 200.1 MHz): δ = 4.33 (m_c, 3 H, 4-H), 2.16 (s, 9 H, 1-Me), 1.79 (dd, J = 4.1, 12.3 Hz, 6 H, *trans*-3-H), 1.48 (dd, J = 11.8, 11.8 Hz, 6 H, *cis*-3-H), 1.08, 0.97 (2 s, 18 H each, *cis*-2-Me, *trans*-2-Me).

^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 65.8 (d, $^2J_{PC}$ = 11.0 Hz, C-4), 55.3 (C-2), 49.0 (d, $^3J_{PC}$ = 2.7 Hz, C-3), 33.3, 20.7 (6 Me each, *cis*-2-Me, *trans*-2-Me), 28.0 (1-Me).

$C_{30}H_{60}N_3O_3P$ (541.8) calcd.: C 66.50 H 11.16 N 7.76

found: C 66.50 H 11.48 N 7.63

Phosphorous acid 2,2,6,6-tetramethyl piperidin-4-yl ester (14)

6.41 g (19.3 mmol) of phosphorous acid monoester diamide **4** were dissolved in 60 ml of dry xylene. 0.70 g (38.9 mmol) of water were added. The reaction mixture was refluxed for 2 h. During cooling to room temperature phosphorous acid monoester **14** precipitated.

Yield: 3.9 g (91%); m.p. 279–82°C (colorless crystals).

^{31}P NMR (D_2O, 121.5 MHz): δ = 3.7 (dd, $^3J_{PH}$ = 9.1 Hz, $^1J_{PH}$ = 637.8 Hz).

^1H NMR (D_2O, 300.1 MHz): δ = 6.79 (d, $^1J_{PH}$ = 637.8 Hz, 1 H, P*H*), 4.64 (m_c, 1 H, 4-H), 2.17 (d, J = 12.4 Hz, 2 H, *trans*-3-H), 1.71 (dd, J = 11.2,

11.2 Hz, 2 H, *cis*-3-H), 1.46 (s, 12 H, *trans*-2-Me, *cis*-2-Me). All signals are very broad.

^{13}C NMR (D_2O, 75.5 MHz): δ = 66.6 (C-4), 58.9 (C-2), 43.0 (br., C-3), 30.6, 26.4 (*trans*-2-Me, *cis*-2-Me).

IR (KBr): $\tilde{\nu}$ = 3450 cm^{-1} (N-H), 2976 (C-H), 2947 (C-H), 2890 (C-H), 2772, 2739, 2678, 2608, 2534, 2489, 2339 (P-H), 1613 (N-H), 1391 (H-C-H), 1231, 1215, 1091, 1052 (P-O-C), 995, 844.

$C_9H_{20}NO_3P$ (221.23) calcd.: C 48.86 H 9.11 N 6.33

found: C 48.24 H 9.34 N 6.29

Phosphorous acid 1,2,2,6,6-pentamethyl piperidin-4-yl ester (15)

0.565 g (31.4 mmol) of water were added to 5.41 g (15.7 mmol) of phosphorous acid monoester diamide **5**. The mixture was stirred for 1h at 90°C. Diethylamine formed was removed in a stream of nitrogen. Afterwards the mixture was heated to 140°C *in vacuo* with continuous stirring. During this procedure phosphorous acid monoester **15** crystallized spontaneously. The crystals were washed with acetonitrile.

Yield: 1.49 g (40.4%); m.p. 224–37°C (colorless crystals).

^{31}P NMR (CD_3OD, 121.5 MHz): δ = −0.4 (dd, $^3J_{PH}$ = 8.8 Hz, $^1J_{PH}$ = 619.6 Hz).

^1H NMR (CD_3OD, 300.1 MHz): δ = 6.92 (d, $^1J_{PH}$ = 619.6 Hz, 1 H, P*H*), 4.68 (m_c, 1 H, 4-H), 2.86 (s, 3 H, 1-Me), 2.36 (dd, J = 4.1, 13.9 Hz, 2 H, *trans*-3-H), 2.11 (dd, J = 12.8, 12.8 Hz, 2 H, *cis*-3-H), 1.59, 1.54 (2 s, 6 H each, *trans*-2-Me, *cis*-2-Me).

^{13}C NMR (CD_3OD, 75.5 MHz): δ = 67.1 (C-2), 65.8 (d, $^2J_{PC}$ = 4.5 Hz, C-4) 47.0 (d, $^3J_{PC}$ = 3.8 Hz, C-3), 30.6, 22.3 (*trans*-2-Me, *cis*-2-Me), 30.4 (1-Me).

$C_{10}H_{22}NO_3P$ (235.26) calcd.: C 51.05 H 9.43 N 5.96

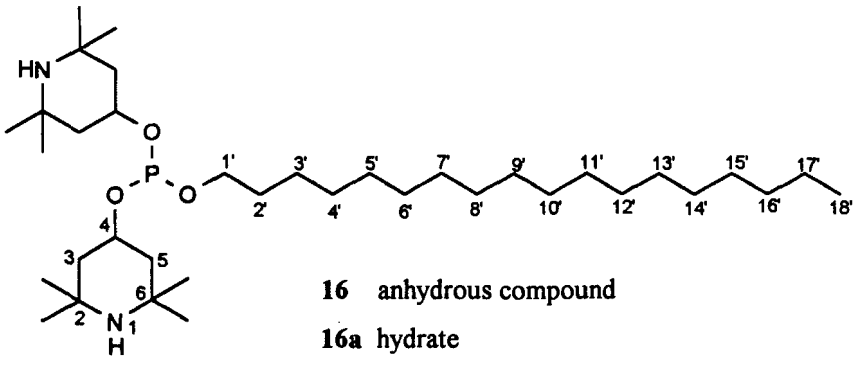
found: C 50.76 H 9.56 N 5.95

Phosphorous acid 1,2,2,6,6-pentamethyl piperidin-4-yl ester × 4 H_2O (15a)

m.p. 80°C (removal of water)....220–40°C (see anhydrous compound **15**)

^{31}P NMR and ^{13}C NMR data are identical with those of the anhydrous compound **15**. The ^1H NMR-spectrum is identical with those of **15** with an additional signal at 4.45 ppm (s, br., 8 H, 4 H_2O).

IR (KBr): $\tilde{\nu}$ = 3460 cm^{-1} (br., O-H, N-H), 3025, 2986 (C-H), 2510, 2381 (P-H), 1677 (N-H), 1506, 1450 (H-C-H), 1399 (H-C-H), 1256, 1214, 1174, 1092, 1077, 1007 (P-O-C), 821.



16 anhydrous compound

16a hydrate

$C_{10}H_{30}NO_7P$ (307.32) calcd.: C 39.08 H 9.84 N 4.56
found: C 38.70 H 9.80 N 4.50

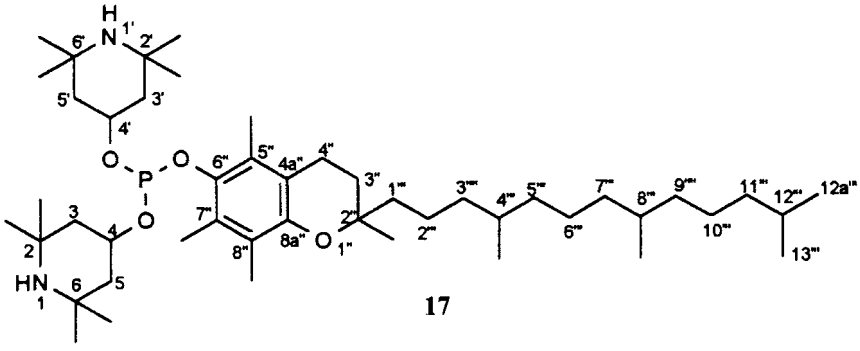
General procedure for the synthesis of phosphites 16–23 containing hindered piperidine groups from phosphorous acid diester monoamides 6 and 7 (GP2)

The phosphorous acid diester monoamides **6** and **7** were mixed with the appropriate amount of the alcohol or phenol, respectively, in a two-neck flask with micro-distillation apparatus attached as described in GP1. The mixture was stirred for a certain time at the temperature reported (see Table I). During that time a weak flow of N_2 was blown through the flask to remove diethylamine formed which was trapped in the cooled distillation receiver to monitor the reaction. The products formed were purified by recrystallization or precipitated as hydrates. In a few cases they were obtained as analytically pure compounds without further purification.

Phosphorous acid bis(2,2,6,6-tetramethyl piperidin-4-yl) stearyl ester (16)

Reaction was carried out according to the general procedure (GP2) with 12.3 g (29.7 mmol) of phosphorous acid diester monoamide **6** and 8.0 g (29.7 mmol) of stearyl alcohol. After the reaction a yellow oil was obtained. The product precipitated as hydrate (**16a**) by adding water to the cooled acetonitrile solution. M.p. 31–36°C (white powder).

The anhydrous compound **16** was obtained as a viscous, yellow oil by dissolving **16a** in *n*-hexane, drying with $MgSO_4$ and evaporating the solvent. Yield: 11.1 g (61%).



17

16

$^{31}P\{^1H\}$ NMR ($CDCl_3$, 81.1 MHz): δ = 138.5.

^1H NMR ($CDCl_3$, 200.1 MHz): δ = 4.46 (m_c, 2 H, 4-H), 3.76 (dt, $^3J_{PH}$ = 6.9 Hz, $^3J_{HH}$ = 6.9 Hz, 2 H, 1′-H), 1.90 (dd, J = 4.2, 12.7 Hz, 4 H, *trans*-3,5-H), 1.57 (m, 2 H, 2′-H), 1.21 (s, 30 H, 3′–17′-H), 1.17, 1.11 (2 s, 12 H each, *cis*-2,6-Me, *trans*-2,6-Me), 0.84 (t, J = 6.8 Hz, 3 H, 18′-H). The signals for 4 H (*cis*-3-H and *cis*-5-H) are completely covered by the singlets at 1.21 ppm and 1.17 ppm.

^{13}C NMR ($CDCl_3$, 50.3 MHz): δ = 67.0 (d, $^2J_{PC}$ = 12.9 Hz, C-4), 61.9 (d, $^2J_{PC}$ = 12.9 Hz, C-1′), 51.7 (C-2, C-6), 46.8 (C-3, C-5, two overlaid doublets, $^3J_{PC}$ not determined), 34.7, 28.8 (4 Me each, *cis*-2,6-Me, *trans*-2,6-Me), 31.7 (C-16″), 31.0 (d, $^3J_{PC}$ = 4.8 Hz, C-2′), 29.6 (C-6′-C-15′), 29.4, 29.3 (C-4′, C-5′), 25.9 (C-3′), 22.6 (C-17′), 14.1 (C-18′).

IR (KBr): $\tilde{\nu}$ = 2956 cm^{-1} (C-H), 2925 (C-H), 2854 (C-H), 1456 (H-C-H), 1376 (H-C-H), 1365, 1237, 1189, 1006 (P-O-C), 982, 837, 759.

Phosphorous acid bis(2,2,6,6-tetramethyl piperidin-4-yl) α-tocopheryl ester (17)

The reaction was carried out according to the general procedure (GP2) with 1.93 g (4.64 mmol) of phosphorous acid diester monoamide **6** and 2.00 g (4.64 mmol) of *rac*-α-tocopherole. Compound **17** was obtained as a viscous, yellowish oil.

Yield: 3.34 g (95%).

$^{31}P\{^1H\}$ NMR ($CDCl_3$, 81.1 MHz): δ = 141.4.

^1H NMR ($CDCl_3$, 200.1 MHz): δ = 4.67 (m_c, 2 H, 4,4′-H), 2.56 (t, J = 6.5 Hz, 2 H, 4″-H_aH_b), 2.21, 2.17, 2.07 (3 s, 3 H each, 5″-Me, 7″-Me, 8″-Me), 2.00 (dd, J = 3.4, 16.0 Hz, 2 H, *trans*-3,3′-or 5,5′-H), 1.78* (dd, J = 3.4, 17.7 Hz,

2 H, *trans*-3,3′-or 5,5′-H), 1.77 (m, 2 H, 3″-H_aH_b), 1.60–1.20 (m, CH_2, tocopheryl, *cis*-3,3′,5,5′-H), 1.17**, 1.15**, 1.12**, 1.10** (4 s, 6 H each, 2,2′,6,6′-Me), 0.84 (d, J = 6.5 Hz, 6 H, 12a‴-H, 13‴-H). *The signal is partly covered by the signal at 1.77 ppm. **Signals for more methyl groups are overlaid.

^{13}C NMR ($CDCl_3$, 50.3 MHz): δ = 147.7 (d, $^5J_{PC}$ = 1.9 Hz, C-8a″), 141.3 (d, $^2J_{PC}$ = 2.4 Hz, C-6″), 127.6 (d, $^3J_{PC}$ = 2.9 Hz, C-5″ or C-7″), 125.6 (d, $^3J_{PC}$ = 3.3 Hz, C-5″ or C-7″), 122.8 (d, $^4J_{PC}$ = 1.6 Hz, C-8″), 117.3 (d, $^4J_{PC}$ = 1.7 Hz, C-4a″), 74.7 (C-2″), 67.6 (d, $^2J_{PC}$ = 10.7 Hz, C-4, C-4′), 51.6, 51.5 (C-2, C-6, C-2′, C-6′), 47.1 (d, $^3J_{PC}$ = 2.4 Hz, C-3, C-3′ or C-5, C-5′), 46.7 (d, $^3J_{PC}$ = 3.4 Hz, C-3, C-3′ or C-5, C-5′), 40.0 39.3 (C-1‴, C-11‴), 37.4, 37.3, 37.25, 37.2 (C-3‴, C-5‴, C-7‴, C-9‴), 34.8, 28.8 (4 Me each, *cis*-2,2′6,6′-Me, *trans*-2,2′,6,6′-Me), 32.7, 32.6 (C-4‴, C-8‴), 31.3 (C-3″), 27.9 (C-12‴), 24.7, 24.5 (C-10‴, C-6‴), 23.7 (2″-Me), 22.7, 22.6 (C-12a‴, C-13‴), 21.0 (C-2‴), 20.8 (C-4″), 19.7, 19.6, (4‴-Me, 8‴-Me), 14.4 (d, $^4J_{PC}$ = 4.9 Hz, 5″- or 7″-Me), 13.5 (d, $^4J_{PC}$ = 5.3 Hz, 5″- or 7″-Me), 11.9 (8″-Me).

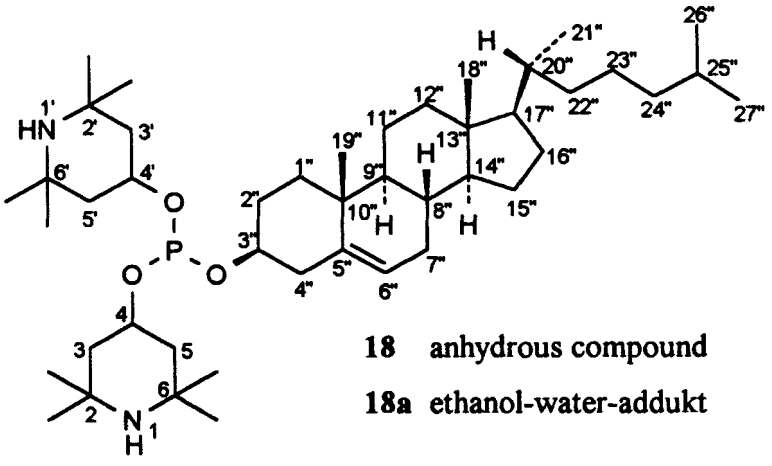
Phosphorous acid bis(2,2,6,6-tetramethyl piperidin-4-yl) cholesteryl ester (18)

The reaction was carried out according to the general procedure (GP2) with 2.4 g (5.8 mmol) of phosphorous acid diester monoamide **6** and 2.3 g (5.8 mmol) of cholesterol. After the reaction a viscous, yellowish oil was obtained. The product was crystallized as an ethanol-water-adduct (**18a**) by adding water to its cooled ethanolic solution. M.p. 41–41.5°C (white powder). The anhydrous compound **18** was obtained as a viscous, yellow oil by dissolving **18a** in toluene, drying with $MgSO_4$ and evaporating of the solvent. It crystallized after weeks and was reprecipitated from acetonitrile to give an oily product first, which crystallized within a week and could be filtered off. M.p. 52–55°C; yield: 3.09 g (73%).

18

^{31}P NMR ($CDCl_3$, 121.5 MHz): δ = 138.8 (dt, $^3J_{PH}$ = 8.5 Hz, $^3J_{PH}$ = 8.5 Hz).

^1H NMR ($CDCl_3$, 200.1 MHz): δ = 5.12 (d, J = 4.8 Hz, 1 H, 6″-H), 4.31 (m_c, 2 H, 4,4′-H), 3.74 (m_c, 1 H, 3″-H), 1.82–1.00 (m, CH_2- and CH-groups, piperidine and cholesterol), 1.00 (s, 12 H, *cis*-or *trans*-2,2′,6,6′-Me), 0.93 (s, 12 H, *cis*-or *trans*-2,2′,6,6′-Me), 0.80 (s, 3 H, 19″- or 18″-H), 0.70 (d, J = 6.4 Hz, 3 H, 21″-Me), 0.65 (d, J = 6.6 Hz, 6 H, 25″-Me), 0.46 (s, 3 H, 19″- or 18″-H).



18 anhydrous compound

18a ethanol-water-addukt

^{13}C NMR ($CDCl_3$, 50.3 MHz): δ = 140.5 (C-5″), 122.0 (C-6″), 73.1 (d, $^2J_{PC}$ = 12.0 Hz, C-3″), 66.8 (d, $^2J_{PC}$ = 11.2 Hz, C-4, C-4′), 56.7 (C-14″), 56.1 (C-17″), 51.6 (C-2, C-2′, C-6, C-6′), 50.1 (C-9″), 46.9 (br, C-3, C-3′, C-5, C-5′), 42.3 (C-13″), 41.2 (d, $^3J_{PC}$ = 3.6 Hz, C-4″), 39.7, 39.5 (C-24″), 37.2 (C-1″), 36.5 (C-10″), 36.1 (C-22″), 35.7 (C-20″), 34.8, 28.9 (4 Me each, *cis,trans*-2,2′6,6′-Me), 31.8 (C-7″), 31.8 (C-8″), 30.7 (d, $^3J_{PC}$ = 3.5 Hz, C-2″), 28.2 (C-12″), 28.0 (C-25″), 24.2 (C-15″), 23.8 (C-23″), 22.8, 22.5 (C-26″, C-27″), 21.0 (C-11″), 19.3 (C-19″), 18.7 (C-21″), 11.8 (C-18″).

$C_{45}H_{81}N_2O_3P$ (729.09) calcd.: C 74.13 H 11.20 N 3.84

found: C 74.25 H 11.26 N 3.46

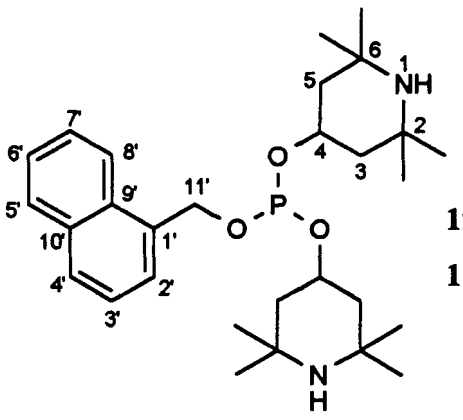
18a

^1H NMR ($CDCl_3$, 200.1 MHz): The signals are identical with those in **18**. Additionally signals are obtained for ~10 H_2O and ~5 EtOH: δ = 4.81 (s, br., 25 H, 10 H_2O, 5 EtO*H*), 3.65 (q, J = 7.0 Hz, 10 H, CH_3CH_2OH), 1.18 (t, J = 7.0 Hz, 15 H, CH_3CH_2OH).

^{13}C NMR ($CDCl_3$, 50.3 MHz): The signals are identical with those in **18**. Additionally signals are obtained for EtOH: δ = 58.1 (CH_2, EtOH), 18.3 (CH_3, EtOH).

Phosphorous acid bis(2,2,6,6-tetramethyl piperidin-4-yl ester) 1(α)-naphthylmethylester (19)

Reaction was carried out according to the general procedure (GP2) with 2.63 g (6.3 mmol) of phosphorous acid diester monoamide **6** and 1.00 g (6.3 mmol) of 1(α)-naphthylmethanol. The mixture was stirred for 8 h at 130 °C. After



19 anhydrous compound

19a monohydrate

cooling a viscous oil was obtained which could be dissolved in acetonitrile and precipitated by addition of water to yield a white crystalline powder which proved to be the hydrate of **19** (**19a**). Yield: 1.3 g (40%); m.p. 33–35°C (white powder).

The anhydrous compound **19** was obtained as an yellowish oil by dissolving **19a** in *n*-hexane, drying with $MgSO_4$ and evaporating the solvent.

19a

$^{31}P\{^1H\}$ NMR ($CDCl_3$, 81.1 MHz): δ = 139.1.

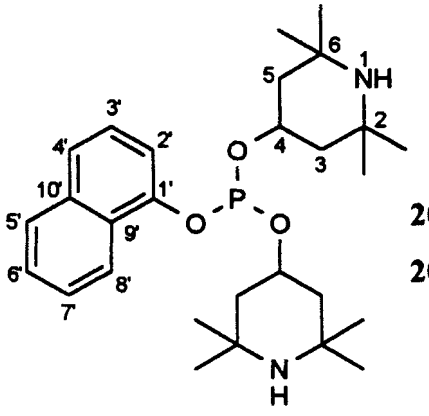
^1H NMR ($CDCl_3$, 200.1 MHz): δ = 8.16–8.10 (m, 1 H, naphthyl), 7.89–7.77 (m, 2 H, naphthyl), 7.57–7.48 (m, 4 H, naphthyl), 5.33 (d, $^3J_{PH}$ = 7.6 Hz, 2 H; 11′-H), 4.47 (m_c, 2 H, 4-H), 1.86 (dd, J = 4.2, 12.4 Hz, 4 H, *trans*-3,5-H), 1.15* (dd, J = 12.4, 12.4 Hz, 4 H, *cis*-3,5-H), 1.11 (s, 12 H, *cis*- or *trans*-2,6-Me), 1.09, 1.08, (2 s, 6 H each, *cis*-or *trans*-2,6-Me).

*The signal is partly covered.

^{13}C NMR ($CDCl_3$, 50.3 MHz): δ = 134.1 (d, $^3J_{PC}$ = 4.2 Hz, C-1′), 133.7 (C-10′), 131.4 (C-9′), 128.6, 126.2, 126.1, 125.5, 125.2, 123.8 (C-2′, C-3′, C-4′, C-5′, C-6′, C-7′, C-8′), 67.6 (d, $^2J_{PC}$ = 13.1 Hz, C-4), 62.0 (d, $^2J_{PC}$ = 7.7 Hz, C-11′), 51.5 (C-2, C-6), 46.8 (d, $^3J_{PC}$ = 2.9 Hz, C-3, C-5), 34.8 (4 Me, *cis*-or *trans*-2,6-Me), 28.79, 28.78 (2 Me each, *cis*-or *trans*-2-Me, *cis*-or *trans*-6-Me).

IR (KBr): $\tilde{\nu}$ = 2956 (C-H), 2928 (C-H), 1600 (=C-H_{ar}), 1500 (=C-H_{ar}), 1463 (H-C-H), 1382 (H-C-H), 1366, 1242, 1190, 1165, 980 (P-O-C), 925, 843, 800, 775.

$C_{29}H_{47}N_2O_4P$ (518.7) calcd.: C 67.15 H 9.13 N 5.40



20 anhydrous compound

20a dihydrate

found: C 66.74 H 8.98 N 5.18

Phosphorous acid bis(2,2,6,6-tetramethyl piperidin-4-yl) 1(α)-naphthylester (20)

The reaction was carried out according to the general procedure (GP2) with 10.9 g (26.2 mmol) of phosphorous acid diester monoamide **6** and 3.8 g (26.2 mmol) of 1(α)-naphthol. After the reaction a viscous oil was obtained which could be dissolved in acetonitrile and precipitated by addition of water to yield a white crystalline powder which turned out to be the dihydrate of **20** (**20a**). M.p. 33–38°C (white powder).

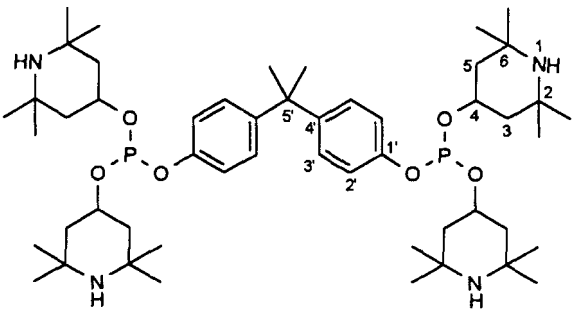
The anhydrous compound **20** was obtained as a viscous, yellow oil by dissolving **20a** in *n*-hexane, drying with $MgSO_4$ and evaporating the solvent. Yield: 3.7 g (29%).

20

^{31}P NMR ($CDCl_3$, 81.1 MHz): δ = 135.5 (d, $^3J_{PH}$ = 5.4 Hz).

^1H NMR ($CDCl_3$, 200.1 MHz): δ = 8.19–8.11 (m, 1 H, 2′-H), 7.77–7.70 (m, 1 H, 8′-H or 4′-H), 7.50–7.13 (m, 5 H, 8′ or 4′, 7′, 6′, 5′, 3′-H), 4.73 (m_c, 2 H, 4-H), 1.92 (m_c, 2 H, *trans*-3- or 5-H), 1.85 (m_c, 2 H, *trans*-5-or 3-H), 1.11, 1.10, 1.08, 1.07 (4 s, 6 H each, *cis*-2,6-Me, *trans*-2,6-Me). The signals for 4 H (*cis*-3-H and *cis*-5-H) are partly covered by the singlets at 1.11–1.07 ppm.

^{13}C NMR ($CDCl_3$, 50.3 MHz): δ = 148.9 (d, $^2J_{PC}$ = 4.8 Hz, C-1′), 134.8 (C-10′), 127.6 (C-5′), 127.4 (d, $^3J_{PC}$ = 1.7 Hz, C-9′), 126.3, 125.6, 125.4 (C-6′, C-3′, C-7′), 122.8 (d, $^4J_{PC}$ = 1.1 Hz, C-8′), 122.3 (C-4′), 113.7 (d, $^3J_{PC}$ =



21 anhydrous compound

21a tetrahydrate

14.7 Hz, C-2'), 68.1 (d, $^2J_{PC}$ = 8.3 Hz, C-4), 51.5 (C-2, C-6), 46.8 (d, $^3J_{PC}$ = 2.7 Hz, C-3, C-5), 34.8, 28.9 (4 Me each, *cis*-2,6-Me, *trans*-2,6-Me).

$C_{28}H_{43}N_2O_3P$ (486.6) calcd.: C 69.11 H 8.91 N 5.76
found: C 69.26 H 9.14 N 5.78

20a

$C_{28}H_{47}N_2O_5P$ (522.7) calcd.: C 64.34 H 9.06 N 5.36
found: C 64.40 H 8.47 N 5.40

(1-Methylethylidene) di-4,1-phenylene phosphorous acid tetrakis(2,2,6,6-tetramethyl piperidin-4-yl ester) (21)

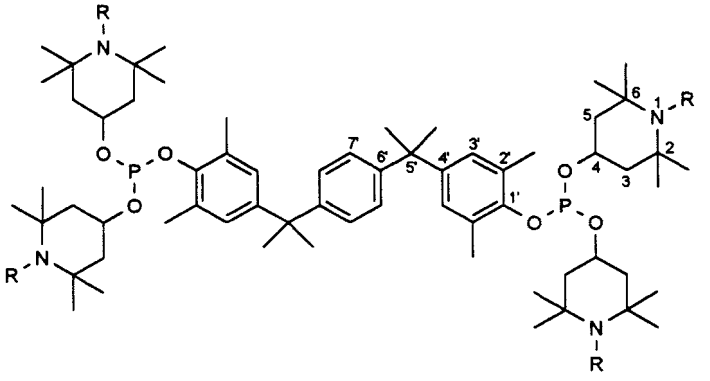
The reaction was carried out according to the general procedure (GP2) with 11.6 g (28.0 mmol) of phosphorous acid diester monoamide **6** and 3.2 g (14.0 mmol) of 2,2-bis(4-hydroxyphenyl)propane. After the reaction an amorphous solid was obtained. The product was crystallized, as the hydrate **21a**, by adding water to the cooled ethanolic solution of the crude product. M.p. 33–36°C (white powder).

The anhydrous compound **21** was obtained as a colorless solid by dissolving **21a** in *n*-hexane, drying with $MgSO_4$ and evaporating the solvent. Yield: 10.1 g (79%).

21

$^{31}P\{^1H\}$ NMR ($CDCl_3$, 81.1 MHz): δ = 135.8.

^1H NMR ($CDCl_3$, 200.1 MHz): δ = 7.10 (d, J = 8.6 Hz, 4 H, 2'- or 3'-H), 6.91 (d, J = 8.6 Hz, 4 H, 2'- or 3'-H), 4.66 (m_c, 4 H, 4-H), 1.90 (dd, J = 3.9, 12.4 Hz, 8 H, *trans*-3,5-H), 1.59 (s, 6 H, 5'-H), 1.15, 1.09 (2 s, 24 H each,



22 R = H
23 R = CH_3

trans,cis- 2,6-Me). The signals for *cis*-3,5-H are covered by the singlet at 1.15 ppm.

^{13}C NMR ($CDCl_3$, 50.3 MHz): δ = 150.6 (d, $^2J_{PC}$ = 6.0 Hz, C-1′), 145.4 (d, $^5J_{PC}$ = 1.2 Hz, C-4′), 127.8 (C-3′), 119.4 (d, $^3J_{PC}$ = 8.1 Hz, C-2′), 67.8 (d, $^2J_{PC}$ = 8.5 Hz, C-4), 51.5 (C-2, C-6), 46.7 (d, $^3J_{PC}$ = 3.0 Hz, C-3, C-5), 41.9 (C-5′), 34.7, 28.9 (*cis,trans*-2,6-Me), 30.9 (5′-Me).

$C_{51}H_{86}N_4O_6P_2$ (913.2) calcd.: C 67.07 H 9.49 N 6.14
found: C 67.20 H 9.94 N 6.38

21a

The ^1H NMR spectrum is identical with those of **21** with an additional peak for ~ 4 × H_2O: δ = 4.9 (s, br., 8 H, 4 H_2O).

1,4-Phenylenebis[(1-methylethylidene)-2,6-dimethyl-4,1-phenylene] phosphorous acid tetrakis(2,2,6,6-tetramethyl piperidin-4-yl ester) (22)

The reaction was carried out according to the general procedure (GP2) with 16.9 g (40.7 mmol) of phosphorous acid diester monoamide **6** and 8.2 g (20.4 mmol) of bisphenol **24**. After the reaction an amorphous solid was obtained. The product was precipitated from acetonitrile. After evaporation of the remaining solvent product **22** was obtained as a white amorphous powder. Yield: 13.3 g (60%); m.p. 57–65°C (white, amorphous powder).

$^{31}P\{^1H\}$ NMR ($CDCl_3$, 81.1 MHz): δ = 139.3.

^1H NMR ($CDCl_3$, 200.1 MHz): δ = 7.07 (s, 4 H, 3′- or 7′-H), 6.83 (s, 4 H, 3′- or 7′-H), 4.66 (m_c, 4 H, 4-H), 2.25 (s, 12 H, 2′-Me), 1.95 (dd, J = 3.6, 12.2 Hz, 4 H, *trans*-3-or 5-H), 1.77 (dd, J = 3.4, 12.6 Hz, 4 H, *trans*-3-or 5-

H), 1.58 (s, 12 H, 5′-Me), 1.19* (dd, 8 H, *cis*-3,5-H), 1.16, 1.14, 1.11, 1.09 (4 s, 12 H each, *cis,trans*-2,6-Me). *Coupling constant was not determined. The signal is largely covered by singlets at 1.16–1.09 ppm.

^{13}C NMR ($CDCl_3$, 50.3 MHz): δ = 147.5 (C-6′), 146.8 (d, $^5J_{PC}$ = 1.4 Hz, C-4′ or $^2J_{PC}$ = 1.5 Hz, C-1′), 145.6 (d, $^2J_{PC}$ = 2.0 Hz, C-1′ or $^5J_{PC}$ = 2.0 Hz, C-4′), 129.5 (d, $^3J_{PC}$ = 2.8 Hz, C-2′), 127.0 (br., C-3′), 126.0 (C-7′), 67.5 (d, $^2J_{PC}$ = 10.3 Hz, C-4), 51.64, 51.58 (C-2, C-6), 46.8 (d, $^3J_{PC}$ = 2.3 Hz, C-3 or C-5), 46.4 (d, $^3J_{PC}$ = 3.1 Hz, C-3 or C-5), 41.7 (C-5′), 34.6, 28.7 (*cis,trans*-2,6-Me), 30.7 (5′-Me), 18.2 (d, $^4J_{PC}$ = 5.9 Hz, 2′-Me or two singlets for two non-equivalent 2′-Me because of hindered rotation).

IR (KBr): $\tilde{\nu}$ = 2967 cm^{-1} (C-H), 2928 (C-H), 2871 (C-H), 1483, 1459 (H-C-H), 1438, 1376 (H-C-H), 1365, 1309, 1236, 1221, 1178, 1121, 1018 (P-O-C), 1003, 980, 952, 903, 870, 834, 763.

1,4-Phenylenebis[(1-methylethylidene)-2,6-dimethyl-4,1-phenylene] phosphorous acid tetrakis(1,2,2,6,6-pentamethyl piperidin-4-yl ester) (23)

The reaction was carried out according to the general procedure (GP2) with 15.4 g (34.8 mmol) of phosphorous acid diester monoamide **7** and 7.0 g (17.4 mmol) of bisphenol **24**. After the reaction an amorphous solid was obtained. The product was recrystallized from acetonitrile/toluene. Yield: 6.8 g (34%); m.p. 177–180°C (colorless crystals).

$^{31}P\{^1H\}$ NMR ($CDCl_3$, 81.1 MHz): δ = 139.3.

^1H NMR ($CDCl_3$, 200.1 MHz): δ = 7.02 (s, 4 H, 3′- or 7′-H), 6.78 (s, 4 H, 3′- or 7′-H), 4.50 (m_c, 4 H, 4-H), 2.21 (s, 12 H, 2′-Me), 2.14 (s, 12 H, 1-Me), 1.83 (m_c, 4 H, *trans*-3-or 5-H), 1.66 (m_c, 4 H, *trans*-3-or 5-H), 1.54 (s, 12 H, 5′-Me), 1.42 (dd, J = 12.1, 12.1 Hz, 8 H, *cis*-3,5-H), 1.07, 1.04, 0.94, 0.92 (4 s, 12 H each, *cis,trans*-2,6-Me).

^{13}C NMR ($CDCl_3$, 50.3 MHz): δ = 147.7 (C-6′), 147.1 (d, $^5J_{PC}$ = 1.5 Hz, C-4′ or $^2J_{PC}$ = 1.5 Hz, C-1′), 145.6 (d, $^2J_{PC}$ = 1.9 Hz, C-1′ or $^5J_{PC}$ = 1.9 Hz, C-4′), 129.7 (d, $^3J_{PC}$ = 2.8 Hz, C-2′), 127.1 (d, $^4J_{PC}$ = 1.3 Hz, C-3′), 126.1 (C-7′), 66.6 (d, $^2J_{PC}$ = 10.1 Hz, C-4), 55.3, 55.2 (C-2, C-6), 49.1 (d, $^3J_{PC}$ = 2.7 Hz, C-3 or C-5), 48.8 (d, $^3J_{PC}$ = 3.5 Hz, C-3 or C-5), 41.8 (C-5′), 33.4, 20.6 (*cis,trans*-2,6-Me), 30.9 (5′-Me), 28.0 (1-Me), 18.2 (d, $^4J_{PC}$ = 5.8 Hz, 2′-Me or two singlets for two non-equivalent 2′-Me because of hindered rotation).

IR (KBr): $\tilde{\nu}$ = 2960 (C-H), 2939 (C-H), 2860 (C-H), 1470 (H-C-H), 1380 (H-C-H), 1310, 1252, 1220, 1177, 1130, 1029, 990 (P-O-C), 970, 957, 905, 895, 870, 840, 800.

$C_{68}H_{112}N_4O_6P_2$ (1143.6) calcd.: C 71.41 H 9.87 N 4.90

found: C 71.56 H 10.19 N 4.71
For X-ray-structure data see.[10]

rac-(±)-Diethyl-phosphoramidous acid 4-(1-{4-[1-(4-hydroxy-3,5-dimethyl-phenyl)-1-methyl-ethyl]-phenyl}-1-methyl-ethyl)-2,6-dimethyl-phenyl ester 2,2,6,6-tetramethyl-piperidin-4-yl ester (24):

13.7 g (34.1 mmol) bisphenol **24** and 11.3 g (34.1 mmol) of phosphorous acid ester amide **4** were dissolved in 250 ml xylene and refluxed for 20 h. Diethylamine formed was removed in a stream of N_2. After evaporating of the solvent a viscous oil remained which crystallized after a few days. The product was recrystallized from *n*-hexane/xylene. Yield: 7.0 g (31%); m.p.148–153°C (colorless crystals).

$^{31}P\{^1H\}$ NMR ($CDCl_3$, 81.1 MHz): δ = 145.6.

^1H NMR ($CDCl_3$, 200.1 MHz): δ = 7.10 (s, 4 H, 3′,12′- or 7′,8′-H), 6.83 (s, 4 H, 3′,12′- or 7′,8′-H), 4.15 (m_c, 1 H, 4-H), 3.21 (m, 4 H, $NCH_aH_bCH_3$), 2.26 (s, 6 H, 2′-or 13′-Me), 2.19 (s, 6 H, 2′-or 13′-Me), 1.94–1.85 (m, 1 H, *trans*-3-or 5-H), 1.81–1.73 (m, 1 H, *trans*-3-or 5-H), 1.62 (s, 12 H, 5′,10′-Me), 1.16, 1.13, 1.11, 1.07 (4 s, 3 H each, 2,6-Me), 1.12 (t, J = 7.1 Hz, 6 H, NCH_2CH_3). Signals for 2 H (*cis*-3,5-H) are covered by singlets at 1.16–1.07 ppm.

^{13}C NMR ($CDCl_3$, 50.3 MHz): δ = 150.0 (C-14′), 148.6 (d, $^2J_{PC}$ not determined, C-1′), 147.8 (C-6′,C-9′), 144.9 (d, $^5J_{PC}$ = 2.1 Hz, C-4′), 142.4 (C-11′), 129.6 (d, $^3J_{PC}$ = 3.0 Hz, C-2′), 127.0 (C-7′, C-8′), 126.2, 126.1 (C-3′, C-12′), 122.3 (C-13′), 68.0 (d, $^2J_{PC}$ = 19.1 Hz, C-4), 51.6, 51.5 (C-2, C-6), 46.9 (d, $^3J_{PC}$ = 3.8 Hz, C-3 or C-5), 46.4 (d, $^3J_{PC}$ = 4.7 Hz, C-3 or C-5), 41.8 (C-5′ or C-10′), 41.6 (C-5′ or C-10′), 38.0 (d, $^2J_{PC}$ = 21.2 Hz, 2 CH_2, NEt_2), 34.9, 34.8, 28.9, 28.8 (4 Me, *cis,trans*-2,6-Me), 30.9 (5′,10′-Me), 18.2 (d, $^4J_{PC}$ = 6.1 Hz, 2′-Me, or two singlets for two non-equivalent 2′-Me because of hindered rotation), 16.1 (13′-Me), 15.0 (d, $^3J_{PC}$ = 3.6 Hz, 2 Me, NEt_2).

IR (KBr): $\tilde{\nu}$ = 2960 (C-H), 2930 (C-H), 2860 (C-H), 1600 (=C-H_{ar}), 1488 (H-C-H), 1454, 1380 (H-C-H), 1305, 1229, 1190, 1125, 1017 (P-O-C), 1000, 935, 905, 880, 845, 817, 800, 764.

$C_{41}H_{61}N_2O_3P$ (660.9) calcd.: C 74.51 H 9.30 N 4.24
found: C 74.52 H 9.65 N 4.09

Acknowledgements

The authors are grateful to SUMITOMO CHEMICAL COMPANY LTD. and CLARIANT HUNINGUE S.A. for financial support of this work. I.B. thanks the 'Freistaat Sachsen' for a predoctoral fellowship. We also thank CLARIANT HUNINGUE S.A., MITSUI PETROCHEMICALS CO. and HÜLS AG for the kind donation of chemicals.

We would like to thank Dr. M. Gruner for recording NMR spectra and Dr. O. Rademacher for performing the X-ray analysis.

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