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Cyclophosphorylation of polyphenols by diamidoarylphosphites

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Abstract—It was found that the cyclophosphorylation of polyphenols by diamidoarylphosphites proceeds via the rupture of only one P–N bond and one P–O bond, the second P–N bond remaining intact. It is supposed that the unusual lack of reactivity of the P–N bond is due to the spatial arrangement of the amido group with respect to the reaction site in phosphorylated intermediates **5**. © 2003 Published by Elsevier Science Ltd.

1. Introduction

This paper deals with the problem of expanding the synthetic use of phosphorus acid amides. These compounds are readily available and have a high phosphorylating capacity of proton-bearing nucleophiles due to the rupture of P–N bonds. They find wide application for the design of different organophosphorus compounds, including complex phosphocyclic systems.[1] Note that phosphorus triamides were predominantly used to obtain phosphocyclanes; aliphatic diamidophosphites found fewer application, and aromatic diamidophosphites were used very rarely.[1] No data are available on the cyclophosphorylation of polyphenols.

When studying the reaction of phosphorus amides with calix[4]resorcinarenes **1**, we found that phosphocyclization of these compounds with aliphatic and aromatic diamidophosphites follows different pathways (Scheme 1).

In the former case, the reaction follows the classical pathway with the rupture of two P–N bonds and formation of phosphocavitands **2**.[2] In the latter case, an anomalous course of the process is observed, which leads to the formation of amidophosphocavitands **3**.[3]

The aim of this work was to elucidate the mechanism of the anomalous cyclophosphorylation and to reveal the limits of its synthetic applications.

2. Results and discussion

2.1. Cyclophosphorylation of calix[4]resorcinarenes

It was found previously that the cyclophosphorylation of calix[4]resorcinarenes with triamides and aliphatic diamidoesters of phosphorus acid is efficiently realized in dioxane at room temperature.[2] These factors favour the stereoselective course of the reaction and convenient separation of the target product from the reaction mixture. Therefore, the reaction of calix[4]resorcinarenes with diamidoarylphosphites was operated in analogous conditions, varying the reagent ratio (**1**:**4**=1:4–8). Calix[4]-resorcinarenes **1a–e** with different hydrocarbon substituents (R) in the bridges between the aromatic rings were used as substrates and diamidoarylphosphites **4a–g** were used as reagents (Table 1).

The process can conventionally be subdivided into two steps (Scheme 1). The first step completely coincides with the classical phosphorylation of alcohols and phenols by phosphorus amides. It includes the rupture of a P–N bond and is completed by the formation of intermediate **5**. In terms of the conventional concepts of diamidophosphite reactivity, the second step, i.e. phosphocyclization of intermediate **5**, should include the rupture of the last P–N bond and afford phosphitocavitands **6**. However, an

Keywords: phenols; calixarenes; phosphoramidites; phosphorylation; cyclization; regiospecificity.

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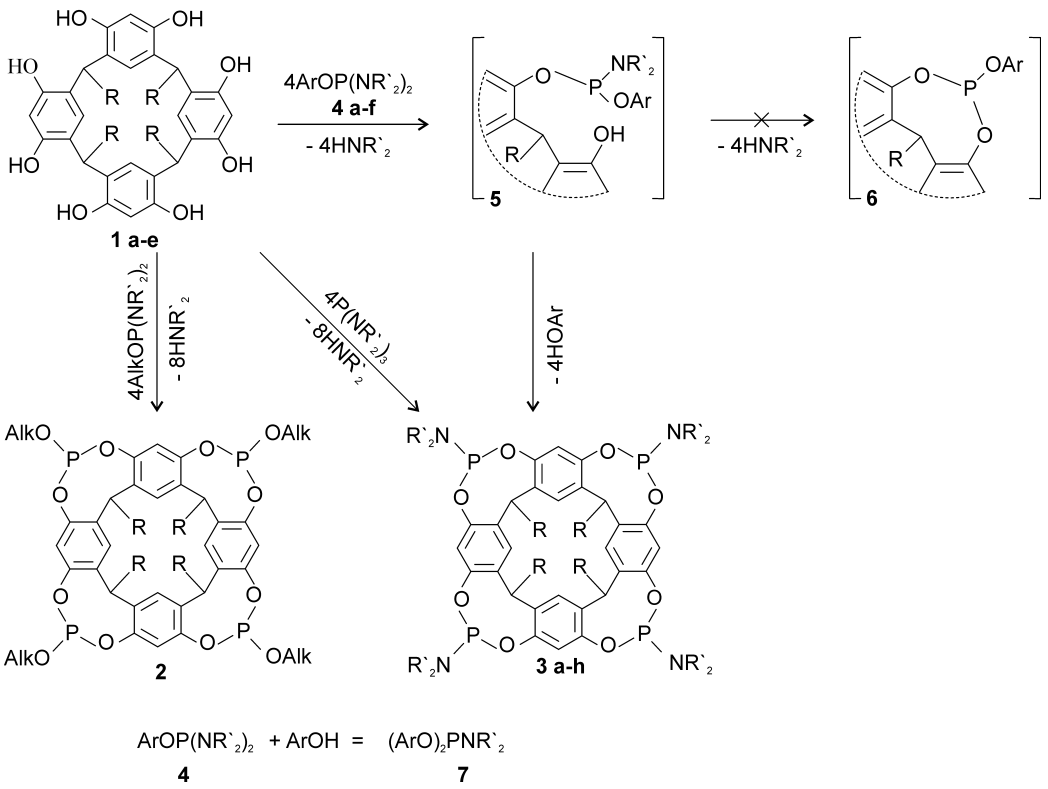


Scheme 1.

anomaly is observed in this case: the rupture of the P–O bond takes place in intermediates **5** at the second step and amidophosphitocavitands **3a–h** are formed. Phosphocavitands **3a–h** are crystallized directly from reaction mixtures as individual symmetric stereoisomers with the equatorial orientation of amide groups at all of the phosphorus atoms.

The composition and structure of compounds **3a–f** were confirmed by the data of elemental analysis and NMR spectroscopy, as well as by the counter synthesis.

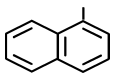
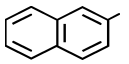
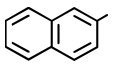
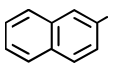
All physicochemical characteristics of these amides coincide with properties of cavitands **3a–f** obtained by the cyclophosphorylation of calix[4]resorcinarenes with phosphorus triamides (Scheme 1, Table 1). The structure and symmetry of the new compounds **3g** and, **3h** were proved by NMR spectroscopy. The spectra of these compounds are typical for symmetric phosphocavitand stereoisomers:[2d,4] a narrow singlet in the ^{31}P NMR spectrum and a set of signals for all protons in the ^{1}H NMR spectrum.

The X-ray structural study of compounds **3e**[3] and, **3f** showed that both molecules are crystallized as dioxane solvates. The main geometrical parameters of **3e** and, **3f** are similar to those of trivalent phosphorus derivatives studied previously (Figs. 1 and 2).[2b,c] All phosphocine cycles exist in a chair–boat conformation with the equatorial orientation of amide groups at the phosphorus atoms. The conformation of *n*-alkyl substituents in the lower rim of the macrocycle deviates from the common all-*trans* conformation because of packing effects. All intermolecular contacts correspond to usual van der Waals interactions.

It is noteworthy that a free phenol (naphthol) is released into the reaction medium at the second stage of the cyclophosphorylation of calix[4]resorcinarenes with diamidoarylphosphites; therefore, the competitive phenolysis (naphtholysis) of the initial diamidophosphite **4** should also be considered (Scheme 1), phenolysis being more rapid than naphtholysis. In our opinion, this is the main factor responsible for the decreased yield of phosphocavitands **3e–h** in the phosphorylation of calixarenes containing phenyl (**1e**) and long alkyl (**1c**,**d**) groups in the lower rim of the macrocycle, with diamidophenylphosphites **4a**,**b** (Table 1). In these cases, along with the signal of cavitand **3** (142–145 ppm), an intense singlet attributed to amidodiarylphosphite **7** (140–141 ppm) is observed in the ^{31}P NMR spectra of reaction mixtures after the completion of the process. It is interesting that no side reactions are observed when calixarenes **1a** and, **b**, which contain small groups in the inter-nuclear bridges, are used. Phenol probably forms inclusion compounds with phosphocavitands **3a–d** and becomes deactivated. The resulting complexes are readily decomposed by ethanol or water. This conclusion is based on the ^{1}H NMR spectroscopic data: along with the proton signals of cavitand **3**, the spectra of products crystallized from the reaction mixtures display signals typical for the protons of free phenol, which disappear after the adduct is decomposed.

The reaction under study has both fundamental and preparative importance. Note that the phosphocyclization of calixarene **1a** with hexaethylphosphorus triamide was completed only when triamide was slowly added to **1a** at 70–80°C. The decrease of temperature and the increase in the concentration of phosphorylating agent resulted in the

Table 1. Synthesis conditions, yields and physicochemical properties of amidophosphocavitands **3**

Calixresorcinarene		Diamidoarylphosphite			Reagent ratio	Reaction duration (days)	Cavitand	Yield (%)
R	No.	Ar	R′	No.				
CH_3	**1a**		CH_3	**4a**	1:4	4	**3a**	72
CH_3	**1a**		C_2H_5	**4b**	1:4	5	**3b**	83
			C_2H_5	**4b**	1:8	5		40
			C_2H_5	**4c**	1:4	5		80
			C_2H_5	**4d**	1:4	11		83
C_3H_7	**1b**		CH_3	**4a**	1:8	4	**3c**	30
C_3H_7	**1b**		C_2H_5	**4b**	1:4	6		58
			C_2H_5	**4d**	1:4	6		84
			C_2H_5	**4e**	1:4	10	**3d**	35
			C_2H_5	**4f**	1:4	14		13
			C_2H_5	**4g**	1:4	17		
C_6H_{13}	**1c**		C_2H_5	**4b**	1:4	11	**3e**	13
			C_2H_5	**4d**	1:4	7		42
C_9H_{19}	**1d**		C_2H_5	**4b**	1:4	14	**3f**	12
C_6H_5	**1e**		CH_3	**4a**	1:8	10	**3g**	8
			C_2H_5	**4b**	1:4	15	**3h**	18

Melting with decomposition.

formation of inseparable mixtures of products containing acyclic (**A**) and cyclic (**B**) phosphorus fragments (Figure 3, Table 2).[2c]

Using diamidoarylphosphites **4**, we achieved the exhaustive cyclophosphorylation of calixarene **1a** by simply mixing the reagents at room temperature. Moreover, phosphocyclization was the principal pathway of the reaction when a double excess of phosphorylating agent was used (**1a**:**4**=1:8) (Table 2).

An example of the preparative effectiveness of diamidoarylphosphites is also provided by the synthesis of C-phenyl derivatives of calixarenes **3g** and, **h** (Scheme 1, Table 1), which could not be obtained using the classical scheme.[2c]

We suppose that the geometry of intermediates **5** is essential for the realization of the effect considered. This supposition is confirmed by the computer simulation of the process. Full geometric optimization of plausible intermediates of the reactions cyclophosphorylation of calixarenes **1** by diamidophosphites has been carried out at semiempirical method AM 1 using GAMESS program package.[5] In intermediates **5**, the phosphorus-bearing group is arranged

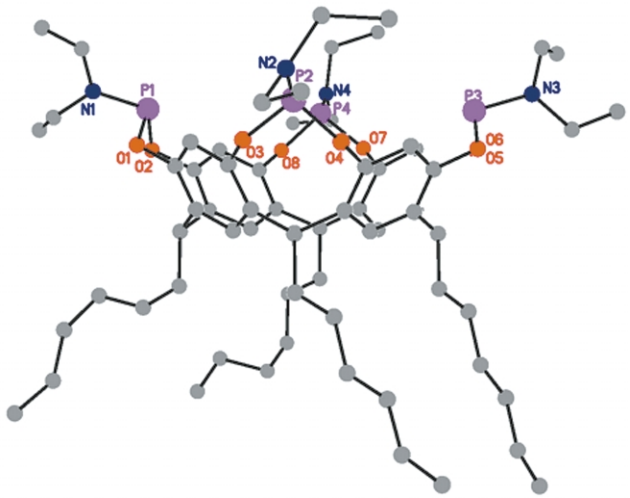


Figure 1. The general view of **3e**. The numbering of the carbon atom and the disorder are omitted for clarity.

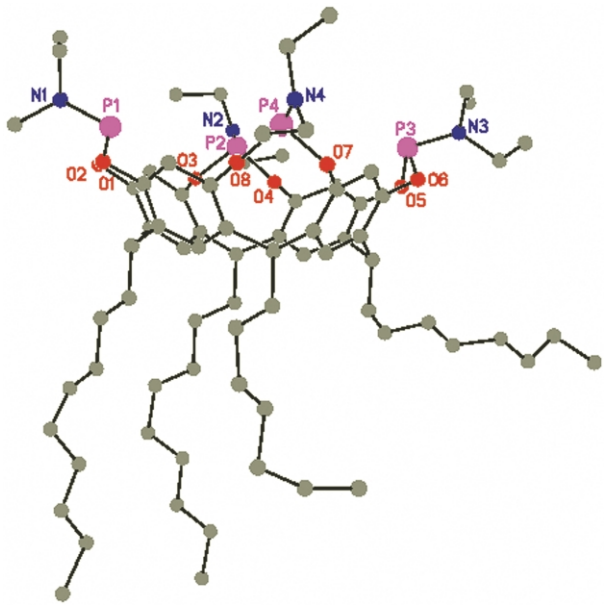


Figure 2. The general view of **3f**. The numbering of the carbon atom and the disorder are omitted for clarity.

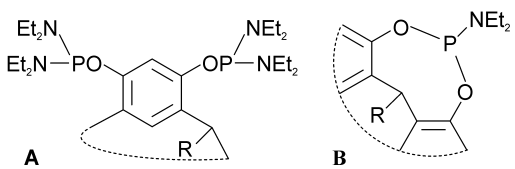


Figure 3. Acyclic (**A**) and cyclic (**B**) phosphorus-bearing fragments formed in the reaction of calix[4]resorcinarenes with phosphorous amides.

in such a way that the phenoxyl group is approached to the hydroxyl group of the adjacent benzene ring and the amido group is moved to the periphery of the system (Fig. 4). This conformation of the intermediate makes possible the intermolecular phosphocyclization due to the rupture of

Table 2. Composition of reaction mixtures in the phosphorylation of calixarene **1a** with phosphorus amides in dioxane at 20°C

1a: Amide	$(Et_2N)_3P$				$(Et_2N)_2POPh$			
	A (%)	δp (ppm)	*B* (%)	δp (ppm)	*A* (%)	δp (ppm)	*B* (%)	δp (ppm)
1:4	64	126.3; 127.6	36	142.6	–	–	100	142.6
1:8	76	126.3; 127.6	24	142.6	30	139.5	70	142.6

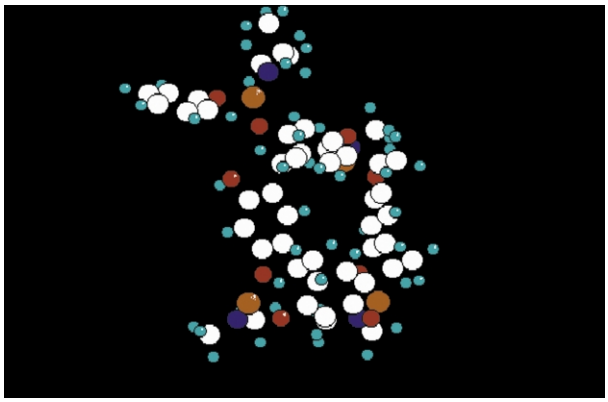


Figure 4. Geometry of a possible intermediate **5** in the cyclophosphorylation of calixarene **1a** by diamidopjosphite **1b**.

the P–O bond alone, i.e. due to reetherification. The unusual lack of reactivity of the P–N bond is due to its position.

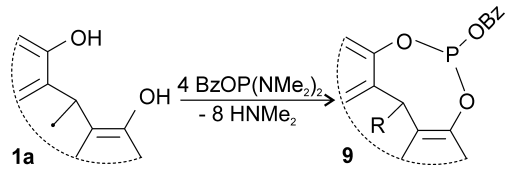
Note that the substitution of the phenyl group in the phosphorylating agent with a benzyl group affects the relative arrangement of interacting groups in intermediates **5**. Experiments on the phosphorylation of calixarene **1a** by diamidobenzylphosphite **8** showed that the reaction follows the classical scheme involving the rupture of two P–N bonds and the formation of phosphitocavitand **9** (Scheme 2).

The reaction was carried out in dioxane and acetonitrile at 25°C. The duration of the reaction was 6 days in dioxane and 24 h in acetonitrile. In the latter case, tetrabenzylphosphocavitand **9** was crystallized from the reaction mixture (Scheme 3).

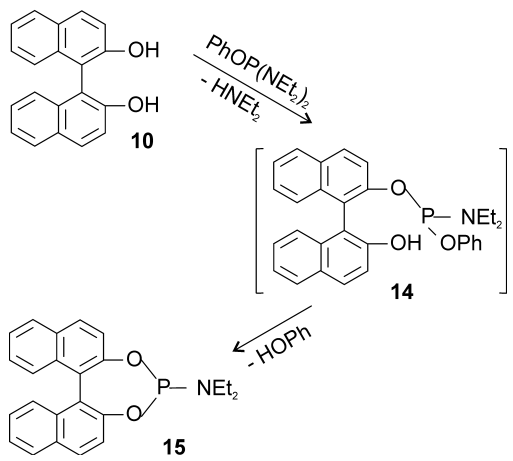
The phosphite nature of phosphocine cycles, the identity of the stereoisomer isolated and the symmetry of the polycyclic skeleton of the molecule were proved by NMR spectroscopy. The ^{31}P NMR spectrum of cavitand **9** displayed a narrow singlet in the characteristic region of neutral phosphites; in the ^{1}H NMR spectrum, no protons signals of diethylamide groups were found, but proton signals of benzyl fragments at the phosphorus atoms were observed with the integral intensities corresponding to the theoretical values.

2.2. Cyclophosphorylation of di- and trihydroxyaromatic compounds

In order to determine the scope of the effect observed, we studied the cyclophosphorylation, under the action of diamidoarylphosphites, of some di- and trihydroxyaromatic



Scheme 2.



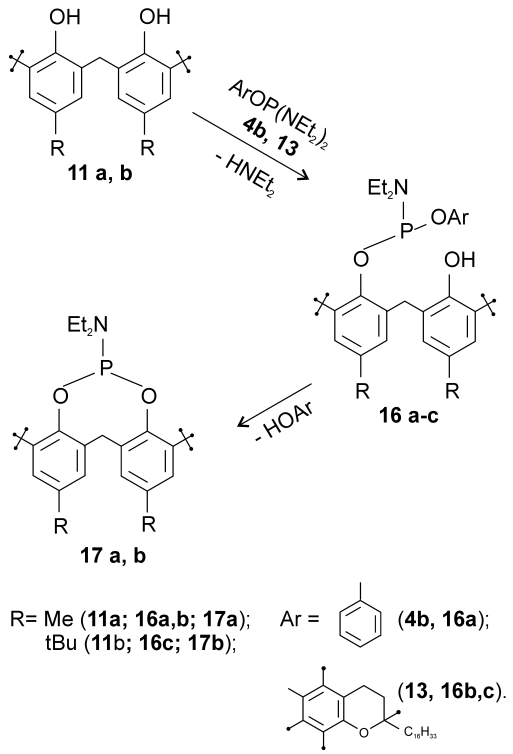
Scheme 3.

systems: 2,2′-dihydroxy-1,1′-bisnaphthyl **10**, 2,2′-methylenebis(6-*tert*-butyl-4alkylphenols) **11a**,**b** and 2,6-bis(3-*tert*-butyl-2-hydroxy-5-methylphenol **12.** Diamidophenylphosphite **4b** and bis(*N*,*N*-diethylamido)-*O*-α-tocopherylphosphite **13** were used as phosphorylating agents. In all cases, reactions were conducted at the equimolar reagent ratio.

Cyclophosphorylation of **10** with diamidophosphite **4b** was achieved in dioxane or acetonitrile in the temperature range 20–80°C. At 20–25°C, the duration of the process was **8** days in dioxane and 24 h in acetonitrile; at 80°C, the reaction was completed in 0.5 h. In all cases, phosphocyclization included the detachment of phenol and formation of dioxaphosphepane **15**. No accumulation of intermediate **14** was observed even at room temperature.

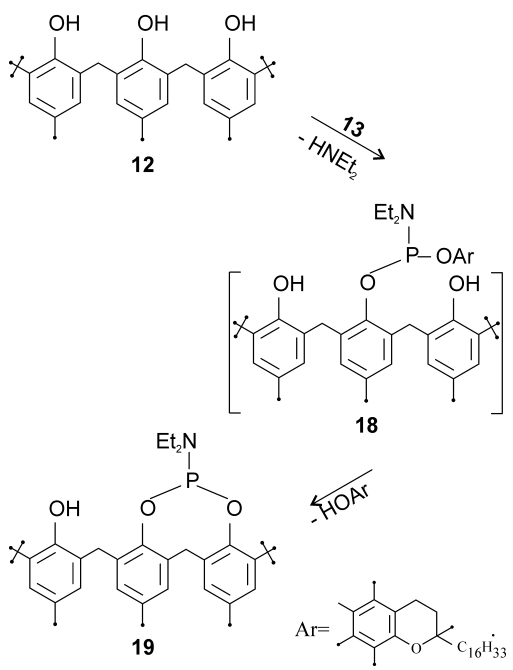
The reaction of methylenebisphenol **11a** with diamidophosphite **4b** (Scheme 4) was conducted under analogous conditions. In this case, monophosphorylated derivative **16a** was the main reaction product at 20–25°C regardless of the solvent. Phosphocyclization was very slow at room temperature because of the presence of bulky *tert*-butyl substituents in the *ortho*-positions of phenolic rings in **11a**; it was completed only when the reaction mixture was heated to 80–100°C and gave dioxaphosphocine **17a**.

When the sterically hindered diamidophosphite **13** was used, the phosphorylation of methylenebisphenols **11a**,**b** proceeded under more severe conditions (120°C, toluene). The reaction gave compounds **16b**,**c**, which were isolated by column chromatography with yields of 90 and 67%, respectively. Heating of monophosphorylated derivatives **16b**,**c** in xylene at 140°C resulted in the detachment of α-tocopherol and formation of dioxaphosphocines **17a**,**b**.



Scheme 4.

The cyclophosphorylation of trisphenol **12** with diamidophosphite **13** (Scheme 5) was carried out in toluene at 120°C. The reaction proceeded analogously to the above processes due to the consecutive ruptures of P–N and P–O bonds and completed by the formation of dioxaphosphocine **19**. Intermediate **18** was not isolated because of its instability.



Scheme 5.

Thus, the revealed phenomenon of intramolecular regulation of the cyclophosphorylation of polyphenols with diamidoarylphosphites is promising for wide synthetic application.

3. Experimental

All syntheses were operated in dry solvents under argon. ^{1}H NMR spectra were recorded with Bruker AC-300 and Bruker WM-200 spectrometers; ^{13}C NMR spectra were recorded with a Bruker AC-300 instrument (75.48 MHz); ^{31}P NMR spectra were recorded with Bruker AC-300 (121.50 MHz) and Bruker WP-80 (32.4 MHz) instruments. MALDI-TOF MS measurements were carried out with Kratos Kompact MALDI II and Kratos Kompact MALDI IV instruments (Shimadzu Europa GmbH). IR spectra were recorded with Nicolet Magna-750 instrument.

Crystallographic data for **3f**: at 110 K crystals of $C_{90}H_{146}N_4O_{12}P_4$ are monoclinic, space group $C2/c$, a=35.486(9) Å, b=26.539(8) Å, c=21.9412(2) Å, β=121.17(1)°, V=17680(9) Å^3, Z=8, M=1599.99, d_{calc}=1.202 g cm^{-3}, μ (Mo K$_\alpha$)=1.46 cm^{-1}, $F(000)$=6960. Intensities of 59191 were measured with a Smart 1000 CCD diffractometer at 110 K (λ(Mo K$_\alpha$)=0.71073 Å, ω-scans with 0.3° step in ω and 30 and 30 s per frame exposure, 2θ<46°) and 12,275 (R_{int}=0.0720) independent reflections were used in further refinement. The structures was solved by direct method and refined by the full-matrix least-squares technique against F^2 in the anisotropic–isotropic approximation. All C_9 substituents with the exception of C62–C70 one, some of Et-groups and for both dioxane solvate molecules are disordered. Due to disorder the positions of oxygen atoms in dioxane molecule have not been located. The refinement of the disordered fragments was carried out in anisotropic (for some atom isotropic) approximation with the restraints on the C–C bond lengths (SAME, DFIX). The hydrogen atoms for the undisordered part were located from electron density synthesis while for the disordered the positions were calculated geometrically. The refinement converged to wR_2=0.3228 and GOF=1.086 for all independent reflections R_1=0.1086 was calculated against F for 8760 observed reflections with $I>2\sigma(I)$). The number of the refined parameters was 1178. All calculations were performed using SHELXTL PLUS 5.1 on IBM PC AT.

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary nos. CCDC-177749. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ UK (Fax: (internat.) +44-1223/336-033; e-mail: deposit @ccdc.cam.ac.uk.

3.1. Cyclophosphorylation of calix[4]resorcinarenes with diamidoarylphosphites: general procedure

A solution of calix[4]resorcinarene **1** (0.4 mmol) and diamidophosphite **4** (1.6 mmol) in dioxane (4 mL) was maintained at 20–25°C for 3–15 days, depending on the reagents used. The precipitate formed was filtered off, washed with dioxane and dried in vacuo.

3.1.1. 1,21,23,25-Tetramethyl-5,9,13,17-tetrakis(dimethylamino)-2,20:3,19-dimetheno-1H,21H,23H,25H-bis[1,3,2λ^3]dioxaphosphocino[5,4-i:5′,4′-i′]benzo[1,2-d:5,4-d′]bis[1,3,2λ^3] benzodioxaphosphocine (3a).[2a] The title compound **3a** is a white solid, mp 270–272°C (decomp.); δ_P (32.4 MHz, $CDCl_3$) 141.3; δ_H (200 MHz, $CDCl_3$) 1.73 (d, $^3J_{HH}$=7.3 Hz, 12H, CH_3), 2.80 (d, $^3J_{PH}$=10.2 Hz, 24H, NCH_3), 4.80 (q, $^3J_{HH}$=7.3 Hz, 4H, CH), 6.49 (s, 4H, *H*o), 7.26 (s, 4H, *H*m).

3.1.2. 1,21,23,25-Tetramethyl-5,9,13,17-tetrakis(diethylamino)-2,20:3,19-dimetheno-1H,21H,23H,25H-bis[1,3,2λ^3]dioxaphosphocino[5,4-i:5′,4′-i′]benzo[1,2-d:5,4-d′]bis[1,3,2λ^3] benzodioxaphosphocine (3b).[2a] The title compound **3b** is a white solid, mp 272–274°C (decomp.); δ_P (32.4 MHz, $CDCl_3$) 142.6; δ_H (200 MHz, $CDCl_3$) 1.17 (t, $^3J_{HH}$=6.7 Hz, 24H, NCH_2CH_3), 1.73 (d, $^3J_{HH}$=7.4 Hz, 12H, CH_3), 3.28 (m, $^3J_{PH}$=9.8 Hz, 16H, NCH_2CH_3), 4.80 (q, $^3J_{HH}$=7.4 Hz, 4H, CH), 6.49 (s, 4H, *H*o), 7.24 (s, 4H, *H*m).

3.1.3. 1,21,23,25-Tetrapropyl-5,9,13,17-tetrakis(dimethylamino)-2,20:3,19-dimetheno-1H,21H,23H,25H-bis[1,3,2λ^3]dioxaphosphocino[5,4-i:5′,4′-i′]benzo[1,2-d:5,4-d′]bis[1,3,2λ^3] benzodioxaphosphocine (3c).[2b] The title compound **3c** is a white solid, mp 260–262°C; δ_P (32.4 MHz, $CDCl_3$) 141.1; δ_H (200 MHz, $CDCl_3$) 1.02 (t, 12H, $CH_2CH_2CH_3$), 1.41 (m, 8H, $CH_2CH_2CH_3$), 2.20 (m, 8H, $CH_2CH_2CH_3$), 2.85 (d, $^3J_{PH}$=10.5 Hz, 24H, NCH_3), 4.68 (t, $^3J_{HH}$=8.0 Hz, 4H, CH), 6.58 (s, 4H, *H*o), 7.20 (s, 4H, *H*m).

3.1.4. 1,21,23,25-Tetrapropyl-5,9,13,17-tetrakis(diethylamino)-2,20:3,19-dimetheno-1H,21H,23H,25H-bis[1,3,2λ^3]dioxaphosphocino[5,4-i:5′,4′-i′]benzo[1,2-d:5,4-d′]bis[1,3,2λ^3] benzodioxaphosphocine (3d).[2b] The title compound **3d** is a white solid, mp 245–247°C; δ_P (32.4 MHz, $CDCl_3$) 142.6; δ_H (200 MHz, $CDCl_3$) 0.99 (t, 12H, $CH_2CH_2CH_3$), 1.18 (t, 24H, NCH_2CH_3), 1.73 (m, 8H, $CH_2CH_2CH_3$), 2.19 (m, 8H, $CH_2CH_2CH_3$), 3.27 (m, $^3J_{PH}$=10.6 Hz, 16H, NCH_2CH_3), 4.62 (t, $^3J_{HH}$=8.0 Hz, 4H, CH), 6.51 (s, 4H, *H*o), 7.13 (s, 4H, *H*m).

3.1.5. 1,21,23,25-Tetrahexyl-5,9,13,17-tetrakis(diethylamino)-2,20:3,19-dimetheno-1H,21H,23H,25H-bis[1,3,2λ^3]dioxaphosphocino[5,4-i:5′,4′-i′]benzo[1,2-d:5,4-d′]bis[1,3,2λ^3] benzodioxaphosphocine (3e).[2d] The title compound **3e** is a white solid, mp 220–223°C; δ_P (32.4 MHz, $CDCl_3$) 142.6; δ_H (200 MHz, $CDCl_3$) 0.91 (t, 12H, $CH_2(CH_2)_4CH_3$), 1.20 (t, 24H, NCH_2CH_3), 1.34 (br, 32H, $CH_2(CH_2)_4CH_3$), 2.23 (m, 8H, $CH_2(CH_2)_4CH_3$), 3.30 (m, $^3J_{PH}$=10.4 Hz, 16H, NCH_2CH_3), 4.61 (t, $^3J_{HH}$=7.8 Hz, 4H, CH), 6.53 (s, 4H, *H*o), 7.14 (s, 4H, *H*m).

3.1.6. 1,21,23,25-Tetranonyl-5,9,13,17-tetrakis(diethylamino)-2,20:3,19-dimetheno-1H,21H,23H,25H-bis[1,3,2λ^3]dioxaphosphocino[5,4-i:5′,4′-i′]benzo[1,2-d:5,4-d′]bis[1,3,2λ^3] benzodioxaphosphocine (3f).[6] The title compound **3f** is a white solid, mp 162–163°C; δ_P (32.4 MHz, $CDCl_3$) 142.7; δ_H (200 MHz, $CDCl_3$) 0.89 (t,

12H, $CH_2(CH_2)_7CH_3$), 1.19 (t, 24H, NCH_2CH_3), 1.28 (br, 56H, $CH_2(CH_2)_7CH_3$), 2.20 (m, 8H, $CH_2(CH_2)_7CH_3$), 3.29 (m, $^3J_{PH}$=10.5 Hz, 16H, NCH_2CH_3), 4.60 (t, $^3J_{HH}$=7.8 Hz, 4H, C*H*), 6.51 (s, 4H, *H*o), 7.12 (s, 4H, *H*m).

3.1.7. 1,21,23,25-Tetraphenyl-5,9,13,17-tetrakis(dimethylamino)-2,20:3,19-dimetheno-1H,21H,23H,25H-bis[1,3,2λ^3]dioxaphosphocino[5,4-i:5′,4′-i′]benzo[1,2-d:5,4-d′]bis[1,3,2λ^3]benzodioxaphosphocine (3g). The title compound **3g** is a rosy solid, mp 217–219°C; [Found: C, 66.49; H, 5.62; N, 5.41; P, 11.19. $C_{60}H_{56}N_4O_8P_4$ requires: C, 66.42; H, 5.20; N, 5.16; P, 11.42 %]; ν_{max} (KBr) 2969, 2849, 1485, 1455, 1151, 1095, 1024, 995, 889, 846, 798, 788, 750 cm^{-1}; δ_P (32.4 MHz, $CDCl_3$) 141.9; δ_H (200 MHz, $CDCl_3$) 2.82 (d, $^3J_{PH}$=10.3 Hz, 24H, NCH_3), 6.26 (s, 4H, C*H*), 6.72 (s, 4H, *H*o), 6.90 (s, 4H, *H*m), 7.14–7.29 (20H, C_6H_5); *m*/*z* 1085 [M$^+$].

3.1.8. 1,21,23,25-Tetraphenyl-5,9,13,17-tetrakis(diethylamino)-2,20:3,19-dimetheno-1H,21H,23H,25H-bis[1,3,2λ^3]dioxaphosphocino[5,4-i:5′,4′-i′]benzo[1,2-d:5,4-d′]bis[1,3,2λ^3]benzodioxaphos-phocine (3h). The title compound **3h** is a rosy solid, mp 230–232°C; [Found: C, 68.44; H, 6.26; N, 4.64; P, 10.01. $C_{68}H_{72}N_4O_8P_4$ requires: C, 68.22; H, 6.06; N, 4.68; P, 10.35%]; ν_{max} (KBr) 2973, 2930, 2877, 1485, 1455, 1151, 1095, 1024, 990, 889, 846, 798, 788, 745 cm^{-1}; δ_P (32.4 MHz, $CDCl_3$) 143.4; δ_H (200 MHz, $CDCl_3$) 1.19 (t, $^3J_{HH}$=7.3 Hz, 24H, CH_3), 3.27 (m, $^3J_{PH}$=10.7 Hz, 16H, NCH_2), 6.25 (s, 4H, C*H*), 6.71 (s, 4H, *H*o), 6.86 (s, 4H, *H*m), 7.06–7.36 (20H, C_6H_5).

3.1.9. 1,21,23,25-Tetramethyl-5,9,13,17-tetrabenzoxy-2,20:3,19-dimetheno-1H,21H,23H,25H-bis[1,3,2λ^3]dioxaphosphocino[5,4-i:5′,4′-i′]benzo[1,2-d:5,4-d′]bis[1,3,2λ^3]benzodioxaphosphocine (9). A solution of **1a** (92.48 mg, 0.17 mmol) and **8** (115.04 mg, 0.68 mmol) in acetonitrile (2 mL) was maintained at 25°C for 24 h. The precipitate was filtered off, washed with dioxane and dried in vacuo. The title compound **9** (88.8 mg, 48%) is a white solid, mp 221–222°C (decomp); [Found: C, 65.89; H, 4.92; P, 10.98. $C_{60}H_{52}O_{12}P_4$ requires: C, 66.18; H, 4.81; P, 11.3%]; ν_{max} (KBr) 2959, 2923, 1488, 1455, 1156, 1096, 1021, 990, 886, 835, 736 cm^{-1}; δ_P (32.4 MHz, $CDCl_3$) 127.5; δ_H (200 MHz, $CDCl_3$) 1.80 (d, $^3J_{HH}$=7.7 Hz, 12H, CH_3), 4.91 (q, $^3J_{HH}$=7.7 Hz, 4H, C*H*), 5.35 (d, $^3J_{PH}$=6.1 Hz, 8H, CH_2), 6.70 (s, 4H, *H*o), 7.32 (s, 4H, *H*m), 7.38–7.48 (20H, C_6H_5).

Tetrathion derivative **9a** was obtained by the sulfurisation of cavitand **9**.

3.1.10. 1,21,23,25-Tetramethyl-5,9,13,17-tetrabenzoxy-5,9,13,17-tetrathion-2,20:3,19-dimetheno-1H,21H,23H,25H-bis[1,3,2λ^3]dioxaphosphocino[5,4-i:5′,4′-i′]benzo[1,2-d:5,4-d′]bis[1,3,2λ^3]benzodioxaphosphocine (9a). A solution of sulfur (13.12 mg, 0.41 mmol) in benzene (2 mL) was added to a solution of **9** (112.06 mg, 0.103 mmol) in chloroform (2 mL). The reaction mixture was stirred at 80°C for 3 h. Two thirds of solvent were removed by distillation in vacuo. The precipitate was filtered off, washed with dioxane and dried in vacuo. The title compound **9a** (110.2 mg, 88%) is a white solid, mp 246–248°C (decomp); [Found: C, 59.02; H, 4.43; P, 10.27. $C_{60}H_{52}O_{12}P_4S_4$ requires: C, 59.20; H, 4.31; P, 10.18%]; ν_{max} (KBr) 2955, 2918, 2849, 1489, 1456, 1280, 1153, 1096, 1024, 997, 920, 885, 875, 755, 733, 694, 674 cm^{-1}; δ_P (32.4 MHz, $CDCl_3$) 58.7; δ_H (200 MHz, $CDCl_3$) 1.79 (d, $^3J_{HH}$=7.1 Hz, 12H, CH_3), 4.85 (q, $^3J_{HH}$=7.1 Hz, 4H, C*H*), 5.37 (d, $^3J_{PH}$=9.4 Hz, 8H, CH_2), 6.64 (s, 4H, *H*o), 7.30 (s, 4H, *H*m), 7.38–7.48 (20H, C_6H_5); *m*/*z* 1242.1 [M+Na$^+$].

3.1.11. Bis(*N*,*N*-diethylamide)-*O*-tocopherylphosphite (13). A mixture of hexaethylphosphorus triamide (24.8 g, 100 mmol) and α-tocopherol (43.1 g, 100 mmol) was heated at 90–100°C. The formed diethylamine was continuously removed by distillation in a slow stream of argon. After 5 h the formation of diethylamine was completed and the reaction mixture was purified in vacuo from residual hexaethylphosphorus triamide and diethylamine and could be used for further reactions. The title compound **13** (60.0 g, 100%) is a yellow oil; [Found: C, 73.54; H, 12.08; N, 4.88. $C_{37}H_{69}N_2O_2P$ requires: C, 73.46; H, 11.50; N, 4.43%]; δ_P (121.5 MHz C_6D_6) 130.33; δ_H (300 MHz C_6D_6): 0.92 (t, $^3J_{HH}$=7.8 Hz, 12H, CH_3 tocopherol side-chain), 1.03 (t, $^3J_{HH}$=7.0 Hz, 12H, $N(CH_2CH_3)_2$), 1.10–1.70 (m, br, 23H, C*H* and CH_2 from tocopherol), 1.20 (s, 3H, CH_3), 2.32 (s, 3H, Ar–CH_3), 2.34 (s, 3H, Ar–CH_3), 2.35 (s, 3H, Ar–CH_3), 2.45 (t, $^3J_{HH}$= 7.0 Hz, 2H, CH_2), 3.04–3.18 (m, 8H, $N(CH_2CH_3)_2$); δ_C (75.48 MHz C_6D_6) 12.91 (Ar–CH_3), 14.33 (d, $^3J_{PC}$= 7.3 Hz, $N(CH_2CH_3)_2$), 15.13 (d, $^3J_{PC}$=7.3 Hz, $N(CH_2CH_3)_2$), 15.80 (d, J_{PC}=7.3 Hz, Ar–CH_3), 20.31–20.49, 21.78 (CH_2), 21.97 (CH_2), 23.30, 23.40, 24.46, 25.42 (CH_2), 25.78 (CH_2), 28.83, 32.38 (CH_2), 33.58, 33.71, 38.23–38.55 (CH_2), 40.39 (d, $^3J_{PC}$=19.9 Hz, $N(CH_2CH_3)_2$), 40.64 (d, $^3J_{PC}$=19.4 Hz, $N(CH_2CH_3)_2$), 75.03 (*tert.-C*), 117.98 (d, J_{PC}=1.6 Hz), 123.33 (d, J_{PC}=1.6 Hz), 126.00 (d, J_{PC}=3.8 Hz), 128.37 (overlapped by signal of C_6H_6), 146.23 (d, $^3J_{PC}$=8.1 Hz), 148.02 (d, J_{PC}=1.9 Hz, Ar–*C*); *m*/*z* 605 [M+H$^+$].

3.1.12. Diethylamido-(1,1′-binaphthalen-2,2′-yl)phosphite (15). A solution of **10** (57.2 mg, 0.2 mmol) and **4b** (53.6 mg, 0.2 mmol) in acetonitrile (1 mL) was maintained at 80°C for 0.5 h. The solvent was half removed by distillation in vaccuo. The precipitate was filtered off, recrystallized from acetonitrile and dried in vacuo. The title compound **15** (63.5 mg, 82%) is a white solid, mp 183–184°C; [Found: C, 74.49; H, 5.62; N, 3.41; P, 8.19. $C_{24}H_{22}NO_2P$ requires: C, 74.41; H, 5.72; N, 3.62; P, 8.00%]; ν_{max} (KBr) 2976, 2964, 2931, 1590, 1503, 1463, 1376, 1327, 1235, 1205, 950, 936, 823, 798, 790, 755 cm^{-1}; δ_P (32.4 MHz, $CDCl_3$) 150.2; δ_H (200 MHz, $CDCl_3$) 1.05 (t, $^3J_{HH}$=7.2 Hz, 6H, NCH_2CH_3), 2.87 (m, $^3J_{PH}$=12.8 Hz, 2H, NCH_2CH_3), 3.04 (m, $^2J_{HH}$=14.1 Hz, $^3J_{PH}$=9.0 Hz, 2H, NCH_2CH_3), 7.23–7.50 (8H, *H*-arom.), 7.80–7.98 (4H, *H*-arom).

3.1.13. Diethylamido-*O*-(2-[2-hydroxy-3-*tert*-butyl-5-methylbenzyl]-4-methyl-6-*tert*-butyl-phenyl)-*O*-phenylphosphite (16a). A solution of **11a** (115.6 mg, 0.34 mmol) and **4b** (91.1 mg, 0.34 mmol) in acetonitrile (1 mL) was maintained at 75°C for 1.5 h. The solvent was removed by distillation and the residue was dried in vacuo. The title compound **16a** (178.3 mg, 98%) is a yellow oil; [Found: C,

74.28; H, 8.97; N, 2.44; P, 8.61. $C_{33}H_{46}NO_3P$ requires: C, 73.99; H, 8.66; N, 2.61; P, 5.78%]; δ_P (32.4 MHz, $CDCl_3$) 147.2; δ_H (200 MHz, $CDCl_3$) 1.15 (t, $^3J_{HH}$=7.3 Hz, 6H, NCH_2CH_3), 1.43 (s, 9H, $C(CH_3)_3$), 1.51 (s, 9H, $C(CH_3)_3$), 2.24 (s, 3H, CH_3), 2.31 (s, 3H, CH_3), 3.32–3.41 (br.m, $^3J_{PH}$=9.4 Hz, $^3J_{PH}$=9.0 Hz, 4H, NCH_2CH_3), 3.97 (d, $^2J_{HH}$=15.4 Hz, 1H, Ar–CH_2–Ar), 4.36 (d, $^2J_{HH}$=15.4 Hz, 1H, Ar–CH_2–Ar), 5.75 (br.s, 1H, O*H*), 6.84 (s, 1H, *H*-arom.), 6.89 (s, 1H, *H*-arom.), 6.95–7.05 (3H, C_6H_5), 7.08 (br.s, 2H, *H*-arom.), 7.23–7.29 (2H, C_6H_5).

3.1.14. Diethylamido-*O*-(2-[2-hydroxy-3-*tert*-butyl-5-methyl-benzyl]-4-methyl-6-*tert*-butyl-phenyl)-*O*-tocopherylphosphite (16b). A solution of **13** (6.05 g, 10 mmol) in toluene (20 mL) was added dropwise to a solution of **11a** (3.40 g, 10 mmol) in toluene (30 mL) and the mixture was refluxed for 24 h. The liquids were removed in vacuo and the residue was purified by column chromatography (bas. Alox, *n*-hexane; R_f=0.4). The title compound **16b** (5.80 g, 66.5%) is a yellow oil; [Found: C, 76.79; H, 10.14; N, 2.01. $C_{56}H_{90}NO_4P$ requires: C, 77.11; H, 10.40; N, 1.61]; δ_P (121.5 MHz, $CDCl_3$) 147.64; δ_H (300 MHz, $CDCl_3$) 0.78 (t, $^3J_{HH}$=6.9 Hz, 12H, CH_3 from tocopherol side-chain), 1.02 (t, $^3J_{HH}$=6.7 Hz, 6H, $N(CH_2CH_3)_2$), 1.10–1.50 (m, br., 21H, C*H* and CH_2 from tocopherol side-chain, 3H, CH_3), 1.26 (s, 9H, $C(CH_3)_3$), 1.37 (s, 9H, $C(CH_3)_3$), 1.60–1.70 (m, br., 2H, CH_2), 1.79 (s, 3H, Ar–CH_3), 1.85 (s, 3H, Ar–CH_3), 1.95 (s, 3H, Ar–CH_3), 2.11 (s, 3H, Ar–CH_3), 2.16 (s, 3H, Ar–CH_3), 2.42 (t, br., 2H, CH_2), 3.00–3.15 (m, br., 2H, $N(CH_2CH_3)_2$), 3.30–3.45 (m, br., 2H, $N(CH_2CH_3)_2$), 84 (d, 1H, $^2J_{HH}$=15.6 Hz, Ar–CH_2–Ar), 4.16 (d, 1H, $^2J_{HH}$=15.6 Hz, Ar–CH_2–Ar), 6.04 (s, 1H, O*H*), 6.67 (s, 1H, Ar–*H*), 6.73 (s, 1H, Ar–*H*), 6.86 (s, 1H, Ar–*H*), 6.96 (s, 1H, Ar–*H*); δ_C (75.48 MHz, $CDCl_3$) 11.88, 12.90, 13.80 (d, $^3J_{PC}$=4.6 Hz, $N(CH_2CH_3)_2$), 14.64, 19.65, 20.81, 20.99 (CH_2), 22.62, 22.72, 23.56 (Ar–CH_3 from bisphenol), 23.93 (Ar–CH_3 from bisphenol and toc-*C*H), 24.45 (CH_2), 24.81 (CH_2), 27.98, 29.59 ($C(CH_3)_3$), 31.25, 31.40 (CH_2), 32.04 (d, $^4J_{PC}$=5.81 Hz, $C(CH_3)_3$), 32.76, 33.79 (Ar–CH_2–Ar), 34.62 ($C(CH_3)_3$), 35.30 ($C(CH_3)_3$), 37.31–37.61 (CH_2), 39.11 (d, $^2J_{PC}$=23.1 Hz, $N(CH_2CH_3)_2$), 39.39 (CH_2), 74.63 (*tert.-C*), 117.4, 122.84, 125.84 (2 s), 126.98, 127.70, 127.83 (d, J_{PC}=3.2 Hz), 127.93, 128.44, 129.09, 132.73, 132.83, 135.93, 141.70 (d, J_{PC}=4.9 Hz), 141.92 (d, J_{PC}=2.2 Hz), 147.49 (d, $^2J_{PC}$=4.5 Hz), 147.68, 151.16 (Ar–*C*); *m/z* 873 [M+H^+], 912 [M+K^+].

3.1.15. Diethylamido-*O*-(2-[2-hydroxy-3,5-di-*tert*-butyl-benzyl]-4,6-di-*tert*-butyl phenyl)-*O*-tocopherylphosphite (16c). A solution of **13** (12.10 g, 20 mmol) in toluene (20 mL) was added dropwise to a solution of **11b** (8.50 g, 20 mmol) in toluene (70 mL) and the mixture was refluxed for 24 h. The liquids were removed in vacuo and the residue was purified by column chromatography (bas. Alox, *n*-hexane). The title compound **16c** (17.3 g, 90.4%) is a colourless oil; [Found: C, 77.69; H, 10.66; N, 1.75. $C_{62}H_{102}NO_4P$ requires: C, 77.86; H, 10.75; N, 1.46%]; δ_P (121.5 MHz, $CDCl_3$) 147.66; δ_H (300 MHz, $CDCl_3$) 0.78 (t, $^3J_{HH}$=7.2 Hz, 12H, CH_3 from tocopherol side-chain), 1.02 (t, $^3J_{HH}$=7.0 Hz, 6H, $N(CH_2CH_3)_2$), 0.90–1.50 (m, br., 21H, C*H* and CH_2 from tocopherol side-chain, 3H, CH_3), 1.11 (s, 9H, $C(CH_3)_3$), 1.19 (s, 9H, $C(CH_3)_3$), 1.27 (s, 9H, $C(CH_3)_3$), 1.39 (s, 9H, $C(CH_3)_3$), 1.60–1.70 (m, br., 2H, CH_2), 1.72 (s, 3H, Ar–CH_3), 1.78 (s, 3H, Ar–CH_3), 1.94 (s, 3H, Ar–CH_3), 2.41 (t, $^3J_{HH}$=6.6 Hz, 2H, CH_2), 3.00–3.15 (m, br., 2H, $N(CH_2CH_3)_2$), 3.30–3.45 (m, br., 2H, $N(CH_2CH_3)_2$), 3.98 (d, 1H, $^2J_{HH}$=16.0 Hz, Ar–CH_2–Ar), 4.16 (d, 1H, $^2J_{HH}$=16.0 Hz, Ar–CH_2–Ar), 5.90 (s, 1H, O*H*), 6.80 (s, 1H, Ar–*H*), 6.91 (s, 1H, Ar–*H*), 7.08 (s, 1H, Ar–*H*), 7.20 (s, 1H, Ar–*H*); δ_C (75.48 MHz, $CDCl_3$) 11.88, 12.54, 13.80 (d, $^3J_{PC}$=4.6 Hz, $N(CH_2CH_3)_2$), 14.74, 19.65–19.75, 20.84 (CH_2), 21.06 (CH_2), 22.63, 22.72, 23.54, 23.93, 24.45 (CH_2), 24.82 (CH_2), 27.99, 29.65 ($C(CH_3)_3$), 30.07, 30.97, 31.32 ($C(CH_3)_3$), 31.53 (CH_2), 31.59, 31.68 ($C(CH_3)_3$), 32.22 (d, $^4J_{PC}$=5.9 Hz, $C(CH_3)_3$), 32.76, 33.79 (Ar–CH_2–Ar), 34.15 ($C(CH_3)_3$), 34.31 ($C(CH_3)_3$), 34.62 ($C(CH_3)_3$), 35.30 ($C(CH_3)_3$), 37.31–37.63 (CH_2), 39.13 (d, $^2J_{PC}$=22.9 Hz, $N(CH_2CH_3)_2$), 39.39 (CH_2), 74.68 (*tert.-C*), 117.45, 121.96, 123.80, 125.03, 125.44, 126.16, 127.89, 128.32, 129.04, 132.22, 135.25, 141.14, 141.42, 141.65, 145.77, 147.45, 147.67, 150.86 (Ar–*C*); *m/z* 957 [M+H^+].

3.1.16. 2-Diethylamino-4,5;7,8-dibenzo-9,9′-di-*tert*-butyl-11,11′-dimethyl-1,3,2-dioxaphosphocin (17a).[7] (a) A solution of **11a** (115.6 mg, 0.34 mmol) and **4b** (91.1 mg, 0.34 mmol) in acetonitrile (1 mL) was maintained at 80–90°C for 10 h.

(b) A solution of **16a** (107.0 mg, 0.2 mmol) in acetonitrile (1 mL) was maintained at 85–95°C for 8 h.

(c) A solution of **16b** (1.00 g, 0.114 mmol) in xylene (15 mL) was heated under reflux for 8 h.

The solvent was removed by distillation. The residue was recrystallized from benzene and dried in vacuo. The title compound **17a** (72 (a), 48.5 (b), and 32.2 (c) mg, 48, 55, and 64% respectively) is a white solid, mp. 136–137°C; [Found: C, 73.13; H, 9.44; N, 3.41. $C_{27}H_{40}NO_2P$ requires: C 73.44 H 9.13 N 3.17%]; δ_P (121.50 MHz, $CDCl_3$) 144.42; δ_H (300.13 MHz, $CDCl_3$) 1.29 (t, $^3J_{HH}$=7.1 Hz, 6 H, $N(CH_2CH_3)_2$),1.40 (s, 18 H, $C(CH_3)_3$), 2.28 (s, 6 H, CH_3), 3.30 (d, $^2J_{HH}$=12.4 Hz, 1 H, *e*-CH_2), 3.43 (p, $^3J_{HH}$=7.1 Hz, 4 H, $N(CH_2CH_3)_2$), 4.35 (dd, $^2J_{HH}$=12.4 Hz, $^5J_{PH}$=2.8 Hz, 1 H, *a*-CH_2), 7.00 (s, 2 H, Ar–*H*), 7.09 (s, 2 H, Ar–*H*); ($_C$ (75.48 MHz, $CDCl_3$) 14.28 (d, $^3J_{PC}$=4.2 Hz, $N(CH_2CH_3)_2$), 20.94 (CH_3), 30.86 (d, J_{PC}=4.2 Hz, $C(CH_3)_3$), 34.61 (CH_2), 34.68 ($C(CH_3)_3$), 38.76 (d, $^2J_{PC}$=21.3 Hz, $N(CH_2CH_3)_2$), 126.28, 128.37, 132.57, 136.30 (d, J_{PC}=3.2 Hz), 141.57 (d, J_{PC}=3.4 Hz), 148.13 (d, J_{PC}=7.9 Hz, C_{aryl}); *m/z* 443 [M+H^+], 370 [M−$HNEt_2$+H^+].

3.1.17. 2-Diethylamino-4,5;7,8-dibenzo-9,9′,11,11′-tetra-*tert*-butyl-1,3,2-dioxaphosphocine (17b).[7] Was obtained from **16c** (1.00 g, 0.1 mmol) analogous to **17a** (c). The title compound **17b** (37.8 mg, 72%) is a white solid, mp 162–163°C; [Found: C, 75.76; H, 10.27; N, 2.74. $C_{33}H_{52}NO_2P$ required: C 75.39 H 9.97 N 2.66%]; δ_P (121.1 MHz, $CDCl_3$) 143.93; δ_H (300.13 MHz, $CDCl_3$) 1.29 (t, $^3J_{HH}$=7.1 Hz, 6 H, $N(CH_2CH_3)_2$), 1.31 (s, 18 H, $C(CH_3)_3$), 1.42 (s, 18 H, $C(CH_3)_3$), 3.39 (d, $^2J_{HH}$=12.4 Hz, 1 H, *e*-CH_2), 3.43 (p, $^3J_{HH}$=7.1 Hz, 6 H, $N(CH_2CH_3)_2$), 4.41 (dd, $^2J_{HH}$=12.4 Hz, $^5J_{PH}$=2.9 Hz, 1 H, *a*-CH_2), 7.24 (d, $^4J_{HH}$=2.3 Hz, 2 H, Ar–*H*), 7.30 (d, $^4J_{HH}$=2.3 Hz, 2 H, Ar–*H*); δ_C (75.48 MHz, $CDCl_3$) 14.40 (d, $^3J_{PC}$=4.3 Hz, $N(CH_2CH_3)_2$), 30.97 (d, J_{PC}=5.1 Hz, $C(CH_3)_3$), 31.52 ($C(CH_3)_3$), 34.40, 35.08

($C(CH_3)_3$), 35.39 (CH_2), 38.86 (d, $^2J_{PC}$=21.3 Hz, $N(CH_2CH_3)_2$), 122.62, 124.75, 135.97 (d, J_{PC}=3.3 Hz), 140.93 (d, J_{PC}=4.2 Hz), 145.69, 148.02 (d, J_{PC}=7.8 Hz, C_{aryl}); *m/z* 526 [M+H$^+$], 453 [M−HNEt$_2$+H$^+$].

3.1.18. Reaction of diamidophosphite (13) with 2,6-bis(2-hydroxy-3-*tert*-butyl-5-methyl-benzyl)-4-methylphenol (12). A solution of **13** (12.10 g, 20 mmol) in toluene (10 mL) was added dropwise to a solution of **12** (1.50 g, 3.30 mmol) in toluene (20 mL) and the mixture was refluxed for 24 h. The liquids were removed in vacuo. The residue was dissolved in 5 mL of methylene chloride and yellowish crystals, identified by NMR as a mixture of **19** and tocopherol, were formed after 20 mL of acetonitrile was added. NMR of compound **19**: δ_P (121.5 MHz, $CDCl_3$) 144.46; δ_H (300 MHz, $CDCl_3$) 1.23 (t, 6H, $N(CH_2CH_3)_2$), 1.30, 1.31 (s, 18H, $C(CH_3)_3$), 2.13, 2.18, 2.19 (s, 12H, CH_3), 3.35–3.44 (m, 4H, $N(CH_2CH_3)_2$), 3.25 (d, $^2J_{HH}$=12.5 Hz, 1H, CH_2), 4.27 (dd, $^2J_{HH}$=12.7 Hz, $^5J_{PH}$=3.0 Hz, 1H, CH_2), 3.47 (d, $^2J_{HH}$=14.6 Hz, 1H, CH_2), 3.93 (d, $^2J_{HH}$=14.6 Hz, 1H, CH_2), 6.59 (1H, O*H*), 6.83–6.94 (6H, Ar–*H*).[8]

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