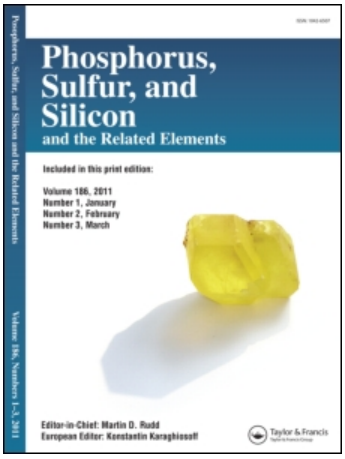

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STERICALLY HINDERED PHOSPHONITES

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STERICALLY HINDERED PHOSPHONITES

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Phosphonochloridous and phosphonous esters were prepared from the reaction of phenylphosphonous dichloride with 2,4-di-*tert*-butylphenol, 2,6-di-*tert*-butyl-4-methylphenol, and 2,4,6-tri-*tert*-butylphenol. Various synthetic methodologies, including phase-transfer catalysis, are described and compared. Phosphonous diesters containing two different substituted-phenyl moieties were prepared from phosphonochloridous monoesters. The reaction of *O*-(2,6-di-*tert*-butyl-4-methylphenyl)-phenylphosphonochloridite with *N*-methyldiethanolamine, *n*-octyl mercaptan, and water was studied and found to give a bisphosphonite, phosphonothioite, and phosphinate, respectively.

The chemistry of phosphonites is well documented in the literature.[1] Quite recently, sterically hindered phosphonite esters have been reported by Spivack and co-workers as stabilizers for polymeric materials.[2] Sterically hindered phosphonites should also prove useful as ligands in transition metal complexes[3,4] since the steric bulk of the ligand is known to affect the phosphorus-metal bond length.[5] Kochi *et al.* have demonstrated steric effects in ligand substitution of metal carbonyls by various phosphine nucleophiles.[6] Neither the preparation nor spectral characterization of hindered phosphonites, however, has appeared in the chemical literature. We report here both synthetic methodology, including solid–liquid phase-transfer catalysis, and spectral characterization of sterically hindered phosphonite esters of *tert*-butyl substituted phenols.

RESULTS AND DISCUSSION

Hoffmann *et al.* have previously reported the preparation of phosphonochloridous esters by the reaction of an equimolar mixture of a phosphonous dichloride, alcohol, and tertiary amine.[7] Since phenolic phosphonites do not readily undergo the Michaelis–Arbusov reaction,[8] the use of an acid acceptor is not necessary.[9] The reaction of 2,4-di-*tert*-butylphenol (**1**) with one equivalent of phenylphosphonous dichloride (**2**) at 50°C gave the phosphonochloridous ester **3** (62% distilled). The analogous reaction of 2,6-di-*tert*-butyl-4-methylphenol (**4a**) with **2** using triethylamine as an acid acceptor gave **5a** (85% recrystallized) although requiring significantly longer reaction times at elevated temperature. A more convenient procedure for the preparation of sterically hindered phosphonochloridous esters was found to

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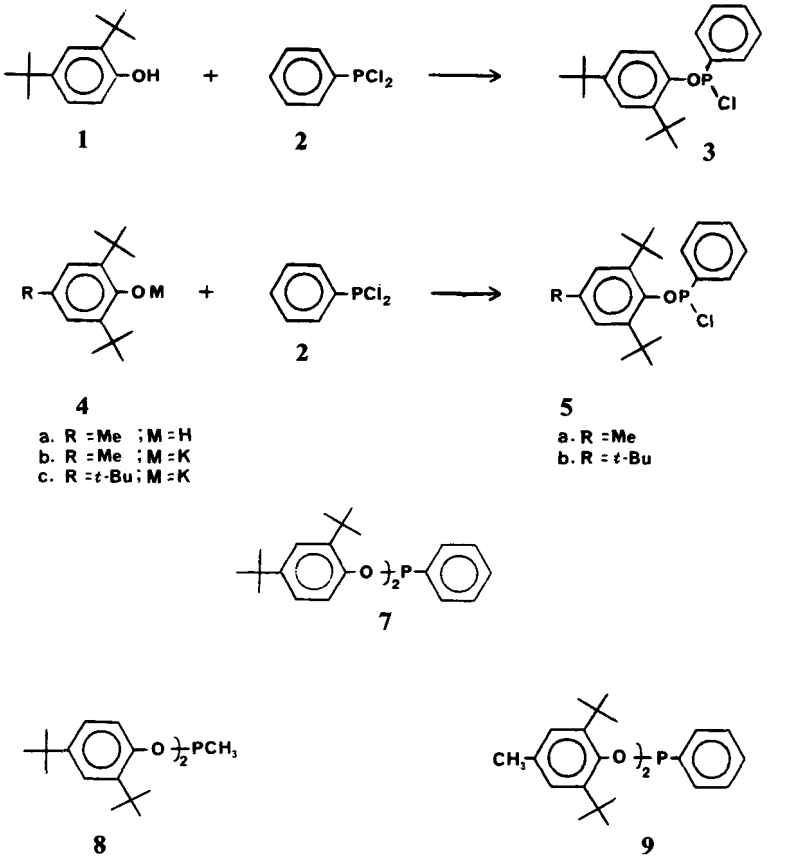
be the reaction of the appropriate phosphonous dichloride with a suspension of the corresponding potassium phenolate in toluene, either with or without a solid–liquid phase-transfer catalyst.[10] The room temperature reaction of a toluene solution of **2** with a suspension of **4b** using N,N,N,N-tetrabutylammonium bromide (**6**) as the phase-transfer catalyst gave **5a** in high yield (78% recrystallized). The analogous reaction of **2** with **4c** without a phase-transfer catalyst produced **5b**, albeit in lower yield (61% recrystallized).

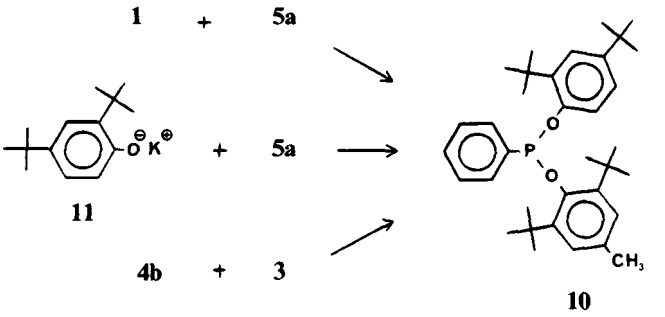


SCHEME 1

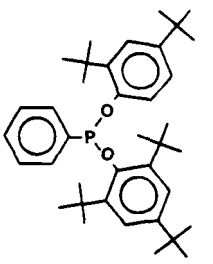
The reaction of a phosphonous dichloride with two equivalents of either an alcohol or a phenol in the presence of a tertiary amine is a general procedure for preparing both cyclic and acyclic phosphonites.[11] The reaction of either phenyl or methylphosphonous dichloride with two equivalents of **1** led to the diesters **7** and **8**, respectively. In contrast to the high yields of **7** and **8** (81% and 80% respectively) obtained by this procedure, the reaction of two equivalents of **4a** with **2** led only to the monoester **5a**. The failure of this procedure to give the desired diester **9** is no doubt due to the increased steric demand brought about by the additional *ortho tert*-butyl substituent of both the phenol **4a** and the intermediate phosphonochlo-

ridous ester **5a**. A low yield (11%) of **9** was obtained by the use of the dipolar aprotic solvent dimethylformamide (DMF) as a cosolvent, which increased not only the dielectric constant of the reaction medium but also the reaction temperature.[12] An improved procedure, which involved the mixing of a suspension of **4b** with a solution of **2** in toluene with a catalytic quantity of DMF, gave a modest yield of **9** (47%). The heterogenous reaction conditions suggest that DMF may be acting as a phase-transfer agent by solubilizing the **4b** in the toluene reaction medium. Although the possibility of a reaction of DMF with **2** to generate a more reactive intermediate was not excluded in the present case, the low yield in the previous case using DMF as a cosolvent strongly suggests that this is not the case.

The ready availability of the phosphonochloridous monoesters **3** and **5a–b** suggested that the preparation of mixed diesters may be possible. The reaction of **5a** with **1** using triethylamine as an acid acceptor gave a low yield of the mixed diester **10**. The reaction of **5a** with the potassium phenolate of 2,4-di-*tert*-butylphenol, **11**, led to an appreciably improved yield of **10** (62% recrystallized). Interestingly, **10** was synthesized in a one-pot procedure by preparing **5a** *in situ* from **4b** and **2** in the presence of the phase-transfer catalyst **6** followed by the addition of **11** (63% recrystallized). An alternate route involving the reaction of **3** with **4b** using **6** as a phase-transfer catalyst led to **10** in slightly higher yield (73% recrystallized). In an analogous manner, **12** was prepared by the reaction of **5b** with **11**.



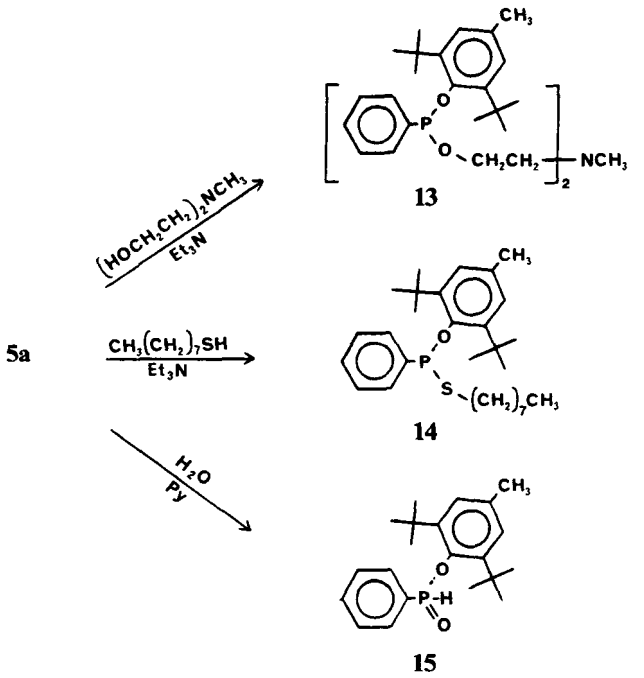
11 **10**



12

SCHEME 2

Although the use of a phase-transfer catalyst in the reactions of this study did not usually result in a significant improvement of yield, the reaction times were greatly reduced. For example, the reaction of **11** with **5a** in the presence of **6** was essentially complete within four hours as determined by TLC, GLC and the IR spectrum of the reaction mixture, although the reaction mixture was often stirred overnight for convenience. Without the phase-transfer catalyst, the reaction times were considerably longer, requiring either greater than **8** hours at room temperature or elevated temperatures.



SCHEME 3

Several other reactions of the phosphonochloridous ester **5a** were explored. Recently, we have reported the reaction of alkanolamines with seven- and eight-membered cyclic phosphorochloridites.[13] The reaction of two equivalents of **5a** with *N*-methyldiethanolamine using triethylamine as an acid acceptor gave the bisphosphonite **13**. The phosphonothioite ester **14** was prepared by the reaction of **5a** with *n*-octylmercaptan using triethylamine as an acid scavenger.[14]

Phosphinic esters are known to be formed by the hydrolysis of phosphonochloridous esters with water in the presence of pyridine.[15] As anticipated, the hydrolysis of **5a** gave the phosphinic ester **15**. The structure of **15** rests on the following observations. The ^{31}P NMR spectrum of **15** has a resonance at δ 22.2, which is in the region expected for a phosphinate. In the ^{1}H NMR spectrum of **15** a doublet resonance was observed at δ 7.99 which was assigned to the proton bonded to phosphorus with $^{1}J_{HP}$ = 555 Hz. The magnitude of $^{1}J_{HP}$ is that expected for the P(V) oxidation state. A PH absorption was observed at 2380 cm^{-1} in the IR spectrum of **15**. These spectral results are fully in accord with the phosphinate structure.

EXPERIMENTAL

All melting points were determined in open capillary tubes on a Thomas–Hoover melting point apparatus and are uncorrected. Boiling points refer to head temperatures and are uncorrected. ^{1}H NMR spectra were taken on a Varian Model CFT-20, XL-100, or XL-200 spectrometer. All ^{1}H shifts are reported relative to tetramethylsilane, where a positive sign is downfield from the standard. ^{31}P NMR spectra were recorded with a Varian Model FT-80 spectrometer equipped with a broad-band probe. ^{31}P chemical shifts are reported in ppm relative to 85% phosphoric acid (external), where a positive sign is downfield from the standard. ^{31}P NMR spectra were acquired using a 45° flip angle, a one second repetition rate with no pulse delay and with full proton decoupling. IR spectra (1% solution in carbon tetrachloride–sodium chloride cells) were recorded on a Perkin–Elmer Model 710 or 467 spectrometer, and reported peak absorptions are estimated to be accurate to ± 10 cm^{-1}. The following qualitative descriptors are used: s = strong, m = medium, w = weak and sh = shoulder. WOELM 04526 silica gel was used for dry-column chromatography. All solvents were dried prior to use. Reagents were purchased from Aldrich Chemical Company. Reactions were carried out in flame-dried apparatus under a dry nitrogen atmosphere. Elemental analyses were performed by Analytical Research Services, CIBA-GEIGY Corporation.

O-(2,4-Di-tert-butylphenyl)-phenylphosphonochloridite (**3**). A mixture of 82.4 g (0.4 mol) of **1** and 74.4 g (0.4 mol) of **2** was heated at 50°C for 6 h (removal of hydrogen chloride was facilitated by a nitrogen sweep of the reaction vessel). The reaction mixture was heated slowly to 90°C, and it was kept at that temperature for 4 h. The reaction mixture was then heated at 50–55°C for 2 h *in vacuo* (0.2 mm) to give 139.8 g of crude product. A 53 g sample was distilled (oil-diffusion pump) to give 33.0 g (62% based upon total sample) of a viscous liquid, bp 142–144°C (0.005 mm).

The product was redistilled to give 8.2 g of viscous liquid which solidified upon standing, bp 145–148°C (0.005 mm); ^{1}H NMR (deuteriochloroform): δ 1.40 (s, $(CH_3)_3C$, 9 H), 1.50 (s, $(CH_3)_3C$, 9 H), 7.00–8.10 (m, ArH, 8 H). Anal. Calcd. for $C_{20}H_{26}ClOP$: C, 68.9; H, 7.5. Found: C, 68.8; H, 7.6.

O(2,6-Di-tert-butyl-4-methylphenyl)-phenylphosphonochloridite (**5a**)

Method A: Phenolate. In a flask equipped with a Dean–Stark trap, a stirred mixture of 22.04 g (0.1 mol) of **4a**, 12.14 g (0.1 mol) of 46.2% aqueous potassium hydroxide, and 130 mL of toluene was heated at reflux until no more water was collected (7 hours). To the resultant phenolate suspension at 5°C was added 0.32 g (1 mmol) of **6** followed by a solution of 17.90 g (0.1 mol) of **2** in 30 mL of toluene. The reaction mixture was stirred overnight at r.t. and then the potassium chloride suspension was removed by filtration. The solvent was removed *in vacuo* and the residue was recrystallized from acetonitrile to give 28.37 g (78%) of a white solid, mp 103–106°C; ^{1}H NMR (deuteriochloroform): δ 1.40 (s, $(CH_3)_3C$, 18 H), 2.32 (s, CH_3, 3 H), 6.78–8.00 (m, ArH, 7 H). Anal. Calcd. for $C_{21}H_{28}ClOP$: C, 69.5; H, 7.8. Found: C, 69.3; H, 7.9.

Method B: Triethylamine. To a solution of 75 g (0.34 mol) of **4a** in 171 g (1.7 mol) of triethylamine at r.t. was added dropwise 60.5 g (0.34 mol) of **2**. The reaction mixture was heated at 90–96°C for 29 hours. The solvent was removed *in vacuo* and the residue was dissolved in a mixture of 150 mL of hexane and 50 mL of benzene. The insolubles were removed by filtration (triethylamine hydrochloride) and the solvent was removed *in vacuo*. The residue was recrystallized from acetonitrile to give 104 g (85%) of a white solid identical in every respect to that prepared by Method A.

O-(2,4,6-Tri-tert-butylphenyl)-phenylphosphonochloridite (**5b**). The procedure of compound **5a** (Method A) was followed using 21.62 g (80 mmol) of 2,4,6-tri-*tert*-butyl phenol, 14.76 g (80 mmol) of **2**, 9.7 g (80 mmol) of 46.3% aqueous potassium hydroxide, and 250 mL of toluene. The residue was recrystallized from acetonitrile to give 22 g (68%) of a white solid, mp 87–93°C; IR: ν 3050 (w), 2970 (s), 2910 (sh), 2870 (m), 1480 (m), 1430 (m), 1400 (m), 1370 (m), 1275 (w), 1245 (w), 1215 (sh), 1200 (m), 1190 (m), 1100 (s), 920 (w), 885 (sh), 860 (s) cm^{-1}.

O-O'-Bis(2,4-di-tert-butylphenyl)-phenylphosphonite (**7**). To a stirred mixture of 41.2 g (0.2 mol) of **1** and 101.2 g (1 mol) of triethylamine at 25–30°C was added dropwise 17.8 g (0.1 mol) of **2** and then the reaction mixture was stirred at 30°C for 15 minutes. The reaction mixture was heated to 65–70°C and it was stirred at this temperature for 6 h, during which time 60 mL of benzene was added to facilitate stirring. The reaction mixture was diluted with an additional 50 mL of benzene and it was poured onto a mixture of 70 g of concentrated hydrochloric acid and 200 g of crushed ice. The mixture was stirred until the ice had melted and it was extracted twice with benzene. The benzene extract was washed with saturated sodium bicarbonate and water, and it was dried over anhydrous sodium sulfate. The solvent was removed *in vacuo* and the residue was recrystallized twice from acetonitrile to give 42.3 g (81%) of a white solid, mp 90–93°C; ^{31}P NMR (deuteriochloroform): δ 155.0; ^{1}H NMR (deuteriochloroform): δ 1.21 (s,

$(CH_3)_3C$, 18 H), 1.27 (s, $(CH_3)_3$, 18 H), 6.80–8.08 (m, ArH, 11 H); IR: 3050 (sh), 2960 (s), 2930 (sh), 2880 (m), 1600 (w), 1490 (s), 1460 (sh), 1420 (sh), 1400 (m), 1360 (m), 1300 (w), 1275 (m), 1240 (sh), 1220 (s), 1190 (s), 1160 (w), 1120 (sh), 1090 (s), 920 (m), 860 (s) cm^{-1}. Anal. Calcd. for $C_{34}H_{47}O_2P$: C, 78.7; H, 9.2. Found: C, 79.0; H, 9.4.

O,O'-Bis(2,4-di-tert-butylphenyl)-methylphosphonite (**8**). By the procedure used to prepare compound **7**, compound **8** was prepared from 12.38 g (60 mmol) of **1**, 6.07 g (60 mmol) of triethylamine, and 3.51 g (30 mmol) of methylphosphonous dichloride.[16] The residue was recrystallized from acetonitrile to give 10.90 g (80%) of a white crystalline solid, mp 102–103.5°C; IR: ν 2980 (s), 2900 (s), 2860 (m), 1480 (s), 1455 (sh), 1390 (m), 1360 (m), 1280 (w), 1230 (s), 1210 (s), 1200 (s), 1150 (w), 1115 (w), 1090 (s), 910 (m), 890 (m), 860 (s) cm^{-1}. Anal. Calcd. for $C_{29}H_{45}O_2P$: C, 76.3; H, 9.9. Found: C, 76.5; H, 9.5.

O-O'Bis(2,6-di-tert-butyl-4-methylphenyl)-phenylphosphonite (**9**)

Method A: Triethylamine/DMF. To a mixture of 22.0 g (1.0 mol) of **4a**, 70.7 g (0.7 mol) of triethylamine, and 20 mL of DMF was added 9.0 g (0.05 mole) of **2**. The reaction mixture was heated at reflux for 22 h. An additional 80 mL of DMF was added and the reaction mixture was heated at reflux (107°C) for an additional 22 hours. The volatiles were removed *in vacuo* and unreacted 2,6-di-*tert*-butyl-4-methylphenol was removed by Kugelrohr distillation (155°C/0.2 mm). The black residue was extracted with 360 mL of hexane at reflux. Upon cooling, the hexane solution was decanted from any insoluble residue which separated. The solvent was removed *in vacuo* and the residue was recrystallized from a 2:1 2-propanol:toluene mixture to give 3.0 g (11%) of a white solid, mp 181–183°C; ^1H NMR (deuteriochloroform): δ 1.24 (s, $(CH_3)_3C$, 36 H), 2.28 (s, CH_3, 6 H), 6.90–7.22 (m, ArH, 9 H); ^{31}P NMR (deuteriochloroform): δ 175.5; IR: ν 3040 (sh), 2950 (s), 2900 (sh), 2860 (m), 1600 (w), 1480 (m), 1435 (m), 1415 (s), 1395 (m), 1360 (m), 1255 (w), 1200 (sh), 1180 (s), 1110 (s), 860 (s) cm^{-1}. Anal. Calcd. for $C_{36}H_{51}O_2P$: C, 79.1; H, 9.4; P, 5.7. Found: C, 78.8; H, 9.4: P, 5.7.

Method B: Phenolate/DMF. In a flask equipped with a Dean–Stark trap, a stirred mixture of 48.5 g (0.22 mol) of **4a**, 27.3 g (0.22 mol) of 45.3% aqueous potassium hydroxide, and 300 mL of toluene was heated at reflux until no more water was collected (6 h). To the reaction mixture at 11°C was added dropwise 17.9 g (0.1 mol) of **2**. The reaction mixture was allowed to warm to room temperature and 3 mL of DMF was added. The reaction mixture was stirred overnight at r.t. and then it was heated at 50°C for three hours. The cooled reaction mixture was extracted sequentially with dilute acetic acid and water, and the organic phase was dried over anhydrous sodium sulfate. The solvent was removed *in vacuo*, and the residue was triturated with 2-propanol. The resultant solid was recrystallized from a 2:1 2-propanol:toluene mixture to give 25.7 g (47%) of a white solid identical in every respect to that prepared by Method A.

O-(2,6-Di-tert-butyl-4-methylphenyl)-O'-(2,4-di-tert-butylphenyl)-phenylphosphonite (**10**)

Method A: Triethylamine. To a stirred solution of 11.60 g (55 mmol) of **1** in 50 mL of triethylamine at 25°C was added dropwise a solution of 19.90 g (55 mmol) of **5a** in 25 mL of toluene. The reaction mixture was heated at reflux for 50 h. The volatiles were removed *in vacuo*. The residue was dissolved in 200 mL of hexane and the triethylamine hydrochloride was removed by filtration. The hexane solution was washed successively with water, 2 M sodium hydroxide, dilute hydrochloric acid (pH = 5), and water, and then it was dried over anhydrous sodium sulfate. The solvent was removed *in vacuo* and the residue was recrystallized sequentially from acetonitrile and a 5:1 acetonitrile:benzene mixture to give 4.37 g (15%) of white crystals, mp 127–129°C; ^1H NMR (deuteriochloroform) (200 MHz): δ 1.37 (s, $(CH_3)_3C$, 9 H), 1.47 (s, $(CH_3)_3C$, 9 H), 1.49 (s, $(CH_3)_3C$, 18 H), 2.37 (s, CH_3, 3 H), 6.55–8.11 (m, ArH, 10 H); IR: ν 3050 (sh), 2960 (s), 2900 (sh), 2870 (m), 1600 (w), 1480 (m), 1460 (sh), 1440 (m), 1420 (s), 1400 (m), 1360 (m), 1280 (sh), 1250 (w), 1220 (sh), 1200 (s), 1180 (s), 1110 (s), 1090 (s), 910 (m), 860 (s). Anal. Calcd. for $C_{35}H_{49}O_2P$: C, 78.9; H, 9.3; P, 5.8. Found: C, 78.7; H, 9.4; P, 6.0.

Method B: Phenolate. In a flask equipped with a Dean–Stark trap, a stirred mixture of 8.24 g (40 mmol) of **1** and 4.85 g (40 mL) of 46.3% aqueous potassium hydroxide was heated at reflux until no more water was collected (6 h). To the cooled reaction mixture at 10°C, a solution of 14.48 g (40 mmol) of **5a** in 40 mL of toluene was added dropwise over a ten minute period. The reaction mixture was stirred for 17 h at r.t. and then the suspension of potassium chloride was removed by filtration. The solvent was removed *in vacuo* and the residue was trituated with acetonitrile. The crude product was recrystallized twice for an acetonitrile:toluene mixture to give 13.1 g (62%) of a white solid, identical in every respect to that prepared by Method A.

Method C: Phase-Transfer Catalysis. In a flask equipped with a Dean–Stark trap, a stirred mixture of 22.2 g (100 mmol) of **4a**, 12.13 g (100 mmol) of 46.2% aqueous potassium hydroxide, and 250 mL of xylene was heated at reflux until no more water was collected (5 h). From the reaction mixture was removed by distillation 50 mL of xylene (via Dean–Stark trap) and to the cooled reaction mixture was added 1.62 g (5 mmol) of **6**. To the reaction mixture at 25°C was added dropwise a solution of 35.0 (95 mmol) of **3** in 40 mL of xylene. The reaction mixture was stirred at r.t. overnight and then it was extracted four times with water. The organic phase was dried over anhydrous sodium sulfate and the solvent was removed *in vacuo*. The residue was recrystallized from acetonitrile to give 36.7 g (73%) of a white solid, identical in every respect to that prepared by Method A.

Method D: One-Pot Procedure. In a flask equipped with a Dean–Stark trap and a bottom outlet, a stirred mixture of 20.63 g (0.1 mol) of **4a**, 12.14 g (0.1 mol) of 46.2% aqueous potassium hydroxide, and 130 mL of toluene was heated at reflux until no more water was collected (7 h). To the resultant phenolate suspension at 10°C was added 0.32 g (1 mmol) of **6** followed by a solution of 17.90 g (0.1 mol) of **2** in 30 mL of toluene and then the reaction mixture was stirred overnight at r.t. The resultant chloridite solution was added through the bottom stopcock into a flask containing a suspension of **11** prepared by azeotropic removal of water from a mixture of 20.63 g (0.1 mol) of **1**, 12.14 (0.1 mol) of 46.2% aqueous potassium hydroxide and 270 mL of toluene. The reaction mixture was stirred four hours and then the precipitate of potassium chloride was removed by filtration. The organic phase was extracted sequentially with 1% aqueous acetic acid, 1% aqueous sodium bicarbonate, and water, and it was dried over anhydrous sodium sulfate. The solvent was removed *in vacuo* and the residue was recrystallized from 2-propyl alcohol to give 29.05 g (63%) of a white solid identical in every respect to that prepared by Method A.

O-(2,4-Di-tert-butylphenyl)-O'-(2,4,6-tri-tert-butylphenyl)-phenylphosphonite (**12**). By the procedure used to prepare compound **10** (Method B), compound **12** was prepared from 10.30 g (50 mmol) of **1**, 6.10 g (50 mmol) of 46.3% aqueous potassium hydroxide and 19.23 g (48 mmol) of **5b**. The reaction mixture was heated to 70–75°C and it was stirred at this temperature for three hours. The reaction mixture was allowed to cool and it was stirred overnight. The suspension of potassium chloride was removed by filtration and the solvent was removed *in vacuo*. The residue was recrystallized from a 5 : 1 acetonitrile : ethyl acetate mixture to give 14.70 g (50%) of white crystals, mp 120–23°C; ^{1}H NMR (deuteriochloroform): δ 1.09 (s, $(CH_3)_3C$, 9 H), 1.19 (s, $(CH_3)_3C$, 9 H), 1.36 (s, $(CH_3)_3C$, 9 H), 1.43 (s, $(CH_3)_3C$, 18 H), 5.38–7.94 (m, ArH, 10 H); IR: ν 2960 (s), 2900 (s), 2860 (m), 1480 (m), 1430 (m), 1390 (w), 1360 (m), 1270 (w), 1220 (s), 1200 (m), 1190 (sh), 1100 (s), 1090 (m), 900 (w), 860 (s), 840 (s) cm^{-1}. Anal. Calcd. for $C_{38}H_{55}O_2P$: C, 79.4; H, 9.7. Found: C, 79.2; H, 9.7.

O-O'(2,2'-N-Methyliminodiethyl)bis[O-(2,6-di-tert-butyl-4-methylphenyl)phenylphosphonite] (**13**). To a solution of 36.3 g (0.1 mol) of **5a** in 100 mL of toluene at 5°C was added sequentially 10.1 g (0.1 mol) of triethylamine followed by 6.0 g (0.05 mol) of 2,2'-*N*-methyldiethanolamine. The reaction was stirred at r.t. until the reaction was complete as indicated by the disappearance of the OH absorption in the IR spectrum. The suspension of triethylamine hydrochloride was removed by filtration and the solvent was removed *in vacuo*. The residue was recrystallized once from acetonitrile and twice from a 10 : 1 acetonitrile : toluene mixture to give 12.5 (32%) of a white solid, mp 98–103°C; ^{1}H NMR (deuteriochloroform): δ 1.40 (s, $CH_3)_3C$, 36 H), 2.05 (s, NCH_3, 3 H), 2.30 (m, NCH_2 and CH_3, 10 H), 3.62 (m, OCH_2, 4 H), 7.20–8.40 (m, ArH, 14 H); IR: ν 1020 (s) cm^{-1} (POC aliphatic stretch). Anal. Calcd. for $C_{47}H_{67}NO_4P_2$: C, 73.1; H, 8.8; N, 1.8. Found: C, 73.4; H, 8.4; N, 1.8.

O-(2,6-Di-tert-butyl-4-methylphenyl)-S-(n-octyl)-phenylphosphonothioite (**14**). To a solution of 7.32 g (50 mmol) of *n*-octylmercaptan and 6.06 g (60 mmol) of triethylamine in 50 mL of toluene at 25° to 28°C was added dropwise to a solution of 18.10 g (50 mmol) of **5a** in 40 mL of toluene. The reaction mixture was heated at 70°C for 6 h. The reaction mixture was extracted sequentially with water, dilute hydrochloric acid, water, 2M sodium hydroxide solution, and water. The organic phase was dried over anhydrous sodium sulfate and the volatiles were removed *in vacuo*. The residue was purified by dry-column chromatography (90 : 10 hexane : benzene eluent) to give 20.8 g (88%) of a colorless liquid; IR: ν 3050 (sh), 2980 (s), 2940 (s), 2870 (m), 1480 (m), 1460 (sh), 1420 (s), 1400 (w), 1260 (w), 1200 (s), 1190 (sh), 1120 (m), 920 (w), 840 (m) cm^{-1}. Anal. Calcd. for $C_{29}H_{45}OPS$: C, 73.7; H, 9.6. Found: C, 73.9; H, 9.5.

O-(2,6-Di-tert-butyl-4-methylphenyl)-phenylphosphinate (**15**). To a solution of 18.14 g (50 mmol) of **5a** and 3.96 g (50 mmol) of pyridine in 100 mL of toluene at 5°C was added 1.8 g (100 mmol) of water. The reaction mixture was stirred at r.t. until disappearance of **5a** as indicated by TLC (approximately seven days). The reaction mixture was extracted with water and the organic phase was dried over anhydrous sodium sulfate. The solvent was removed *in vacuo* and the residue was recrystallized twice from acetonitrile to give 11.0 g (64%) of white crystals, mp 132–133°C; ^{31}P NMR (deuteriochloroform): δ 22.2; ^{1}H NMR (deuteriochloroform): δ 1.46 (s, $(CH_3)_3C$, 18 H), 2.33 (s, CH_3, 3 H), 7.15–7.96 (m, ArH, 7

H), 7.99 (d, PH, $^1J_{HP}$ = 555 Hz, 1 H); IR: ν 2380 (PH), 900 (P(=O)H) cm^{-1}. Anal. Calcd. for $C_{21}H_{29}O_2P$: C, 73.2; H, 8.5. Found: C, 73.6; H, 8.3.

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