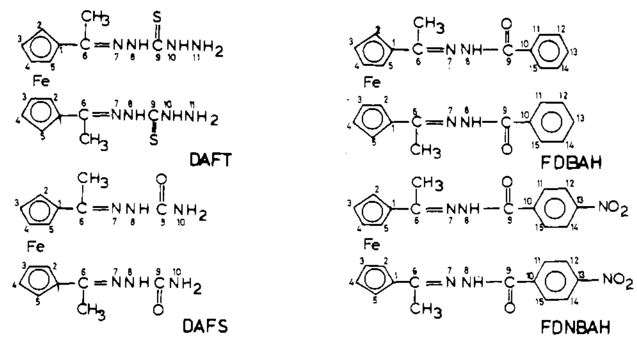

Figure 1.

spectrum of the four compounds showed absorptions in the region 451-456 nm assignable to n-π^* transition.

Elemental analyses were submitted for review.

Registry No. DAFT, 113219-05-9; DAFS, 113219-06-0; FDBAH, 113219-07-1; FDNBAH, 113219-08-2; BAH, 613-94-5; NBAH, 636-97-5; DAF, 1273-94-5; TCH, 2231-57-4; SCH, 563-41-7; ethyl benzoate, 93-89-0; ethyl *p*-nitrobenzoate, 99-77-4.

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Preparation of Sterically Hindered Phosphoramidates

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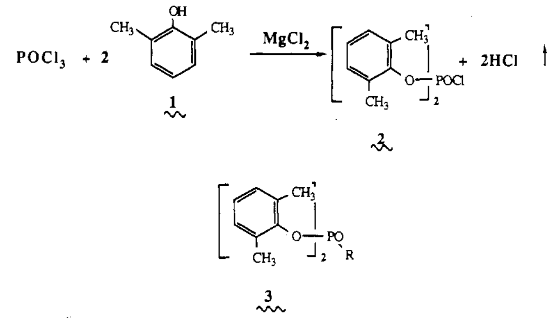
Treatment of phosphorus oxychloride with two equivalents of 2,6-dimethylphenol in the presence of magnesium chloride produced the sterically hindered bis(2,6-dimethylphenyl) chlorophosphate in excellent yield. The diaryl phosphorochloridate reacted with a variety of primary and secondary amines to produce phosphoramidates in good to excellent yield.

We recently required a synthesis of a diaryl chlorophosphate that gave product of high purity and high overall yield without an elaborate purification scheme. We found that treatment of phosphorus oxychloride with two equivalents of the sterically hindered phenol, 2,6-dimethylphenol (**1**), in the presence of a catalytic amount of magnesium chloride produced bis(2,6-dimethylphenyl) chlorophosphate (**2**) in excellent yield (Scheme I). The crude reaction mixture contains esentially pure **2** and can easily be purified by simple distillation, bp 165 °C/1 mm in 90-95% isolated yield. Pure **2** is quite stable providing the necessary precautions are taken to prevent its exposure to excessive moisture.

The hydrolysis product of **2**, bis(2,6-dimethylphenyl) hydrogen phosphate (**3a**) (*1*, *2*) and the adduct from **2** with benzylamine (**3b**) (*1*) have been described previously; however in neither case was **2** actually isolated. In spite of the very hindered nature of **2**, it is readily converted to phosphoramidates and bis(phosphoramidates) upon treatment with a variety of primary and secondary amines and diamines in the presence of triethylamine. Presented in Table I is a list of some representative phosphoramidates prepared from **2**. The products were identified by their spectral data (see Table II), and melting points. For all new compounds satisfactory high-resolution mass spectral data as well as correct elemental analyses were obtained.

Scheme I



Experimental Section

Melting points were determined on a Thomas Hoover apparatus and are uncorrected. Infrared spectra were determined with a Beckman Microlab MX-250 spectrophotometer as KBr disks; absorbance positions are reported in reciprocal centimeters (cm^{-1}). Proton magnetic resonance spectra were recorded on Varian EM-390 spectrometer as solutions in chloroform-*d* unless otherwise stated. High-resolution mass spectra were recorded on a MAT instrument. Elemental analyses were determined by the General Electric analytical services group.

Preparation of Bis(2,6-dimethylphenyl) Chlorophosphate. A mixture of 2,6-dimethylphenol (484 g, 4.0 mol) and phosphorus oxychloride (307 g, 2.0 mol) containing anhydrous magnesium chloride (9.5 g, 0.1 mol) was heated to 150 °C over a 4-h period. During the heating period a copious amount of hydrochloric acid gas was evolved and the solution aquired a light brown color. After the gas evolution ceased, the residue was distilled under reduced pressure to provide 598 g, 92% of pure **2**, bp 165 °C/1 mm, which solidified upon standing, mp ca. 50 °C.

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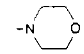
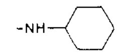
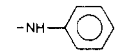
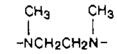
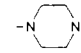
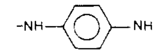
Table I. Representative Derivatives Prepared from Bis(2,6-dimethylphenyl) Chlorophosphate

compd. no.	R	yield,[a] %	mp, °C	mass spectrum[b] M$^+$ calcd	mass spectrum[b] M$^+$ found
3a	-OH	89	141-142 [lit. 141-142] (*1*)		
3b	$-NHCH_2C_6H_5$	88	119.5-121.0 [lit. 120-121.5] (*1*)		
3c		80	166-167	375.1599	375.1586
3d		74	126-127	387.1963	387.1979
3e		90	163-164	381.1491	381.1490
3f	$-NHCH_2CH_2NH-$	68	202-204	636.2518	636.2518
3g	 $-N(CH_3)CH_2CH_2N(CH_3)-$	78	230.5-231.5	664.2831	664.2824
3h		68	195-196	662.2675	662.2669
3i		61	237-239	684.2518	684.2541

[a] Yield of isolated purified material. [b] Elemental analyses (C, H, N, P) were submitted for review and agreed with the appropriate theoretical values.

Table II. Spectral Data of Phosphoramidates

compd no.	IR, cm^{-1}	^1H NMR, ppm
3c	1470, 1260, 1164, 980, 933, 915, 778	2.27 (m, 12 H); 3.43 (m, 4 H); 3.67 (m 4 H); 6.97 (s, 6 H)
3d	3260, 2930, 1470, 1450, 1253, 1170, 1100, 945, 768	0.87-2.07 (m, 10 H); 2.30 (s, 12 H); 2.76 (m, 1 H, exchanges with D_2O); 3.23 (m, 1 H); 7.00 (s, 6 H)
3e	1228, 1143, 1086, 971, 933, 903, 746	2.21 (s, 12 H); 6.97 (s, 6 H); 7.21 (m, 6 H)
3f	3187, 1460, 1252, 1187, 1163, 1119, 1087, 925, 782	2.23 (s, 24 H); 3.17 (m, 4 H); 4.00 (m, 2 H); 6.97 (s, 12 H)
3g	1467, 1265, 1174, 1156, 1004, 929, 913, 786, 764	2.20 (s, 24 H); 3.05 (d, 6 H, J = 10 Hz); 3.45 (d, 4 H, J = 10 Hz); 6.95 (s, 12 H)
3h	1467, 1262, 1183, 1156, 1086, 971, 923, 775, 689	2.27 (s, 24 H); 3.40 (dd, 8 H, J_{P_1H} = 10 Hz, J_{P_2H} = 1.5 Hz); 7.00 (s, 12 H)
3i[a]	1253, 1216, 1165, 1148, 983, 937, 767	2.20 (s, 24 H); 7.04 (s, 12 H); 7.06 (s, 4 H); 8.69 (d, 2 H, J = 10 Hz, exchanges with D_2O)

[a] NMR in methyl-d_6 sulfoxide.

Preparation of Bis(2,6-dimethylphenyl) N-Benzylphosphoramidate (3b): Typical Example. To a stirred solution of bis(2,6-dimethylphenyl) chlorophosphate (182 g, 0.56 mol) in 250 mL of chloroform was added a solution of benzylamine (60 g, 0.56 mol) and triethylamine (61 g, 0.60 mol) in 100 mL of chloroform over a 2-h period at room temperature. After the addition was complete, the solution was heated to reflux for 3 h and then cooled to room temperature. The reaction mixture was diluted with chloroform, washed with 3 N hydrochloric acid and brine, dried over anhydrous magnesium sulfate, filtered, and concentrated. The crude solid was taken up in boiling *n*-heptane and allowed to cool whereupon crystals of pure **3b** formed, which were isolated by filtration, 195 g, 88%, mp 119.5-121.0 °C [lit. (*1*) mp 121.0-121.5 °C].

Registry No. 1, 576-26-1; 2, 81639-99-8; **3a**, 18350-99-7; **3b**, 18350-95-3; **3c**, 113088-99-6; **3d**, 113089-00-2; **3e**, 113089-01-3; **3f**, 113089-02-4; **3g**, 113089-03-5; **3h**, 113089-04-6; **3i**, 113089-05-7.

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