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Reaction of O,O-Dialkyl Alkylphosphonates with Thionyl Chloride. A Remarkable Effect of the O-(2-Dialkylamino)ethyl Substituent

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ABSTRACT

Reaction of dialkyl alkylphosphonates with $SOCl_2$ in the presence of DMF, reported by Maier, can serve as a convenient route to simple monoalkyl alkylphosphonochloridates. However, when a substrate contains a (2-dialkylamino)ethyl group as one of the ester functions, the course of the reaction is determined by the nature of the N-alkyl groups. With the NMe_2 group present, reaction with $SOCl_2$ occurs at nitrogen, and no exchange of groups at phosphorus takes place. The NEt_2 group, on the other hand, directs the reaction to phosphorus, and the Maier reaction of the exchange of one ester group OR for Cl proceeds in high yields. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

One of the general methods for the preparation of phosphonyl dichlorides, important synthetic intermediates, is based on the reaction of the corresponding O,O-dialkyl esters (1) with chlorinating agents, particularly with PCl_5 [1]. A useful variation of the method involves the application of bis(trimethylsilyl) phosphonates as substrates [2], but the major advancement was achieved by Maier, who reported the catalytic effect of N,N-disubstituted formamides on the conversion of dialkyl phosphonates into chlorides by their reaction with $SOCl_2$ [3]. Although there is no doubt that all those reactions involve the formation of the monoesters-monochlorides, R-P(O)(OR′)Cl (2), as intermediates, the latter compounds are not easily prepared by that method or, for that matter, by any other method. Early claims of high (61–93%) yields of compounds 2 obtained by treatment of the diesters with $SOCl_2$ or by $(COCl)_2$ [4] must be treated with skepticism, as the molecular refractivities and chlorine elemental analysis were given as sole evidence for the identity and the purity of the products. Maier [3] reported serious problems with the isolation of the monochlorinated products in the reaction of 1 with the $SOCl_2$/DMF system due to their propensity to thermal decomposition.

In our recent study on the fragmentation of (2-dialkylamino)ethyl phosphonic derivatives [5], we were in a need of substrates 2 bearing a (2-dialkylamino)ethyl substituent as the ester group (2, R′ = $CH_2CH_2NR''_2$). In this article, we report our attempts to prepare such substrates via the chlorination of the corresponding mixed O-alkyl,O′-(2-dialkylamino)ethyl alkylphosphonates and the effect of the nitrogen substituents on the course of the reaction.

RESULTS AND DISCUSSION

Maier's procedure for the preparation of monochlorides 2 (refluxing of 1 with 2.5 mol-equiv. of $SOCl_2$ in the presence of 1-5 mol% DMF for 2.5 hours [3]) was first tested on some simple dialkyl alkylphosphonates (Table 1). It is obvious from the result obtained for 1a that the low yield reported be-

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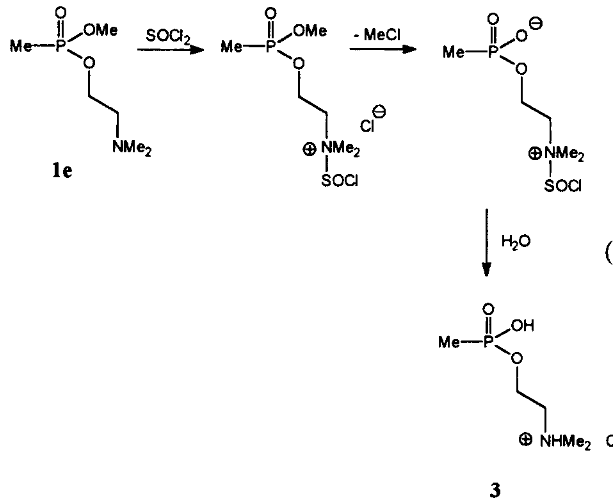
fore [3] was a consequence of the partial decomposition during the distillation. It also seems that the high yields reported for **2b** and **2c** [4] are inconsistent with pure products in view of the high temperature at which they were distilled. It seems, however, that Maier's procedure is a perfectly acceptable method for preparing simple phosphonochloridates **2**, provided that the products are purified by distillation at the lowest possible temperature.

We applied the same procedure to alkylphosphonic diesters containing the (2-dialkylamino)ethyl group as one ester functionality. We have found that the reaction products depend on the nature of the alkyl group of the second ester function, as well as on the nature of the alkyl substituents at nitrogen. The first substrate used was methyl (2-dimethylamino)ethyl methylphosphonate (**1e**). A precipitate formed; NMR spectroscopy showed that no P(O)Cl functional group was present (^{31}P NMR) and that the methyl ester group has been cleaved (^{1}H NMR). Upon hydrolysis (D_2O), the product was identified as the hydrochloride salt of (2-dimethylamino)ethyl methylphosphonic acid (**3**), formed via the nucleophilic demethylation of the P-OMe function [6]. The structure of **3** was confirmed by the independent preparation of the salt and by the comparison of the reaction product with the authentic sample. Taking into consideration a report on the formation of the ionic products from $SOCl_2$ and tertiary amines [7], we believe that the reaction of **1e** can be presented as in Equation 1.



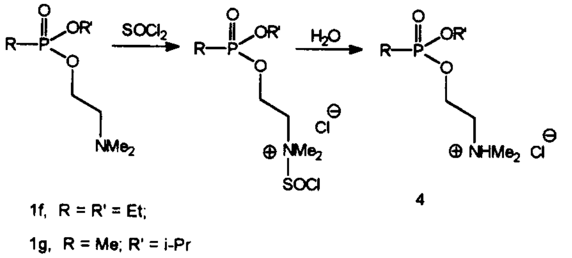
(1)

When ethyl (2-dimethylamino)ethyl ethyl phosphonate (**1f**) and *i*-propyl (2-dimethylamino)ethyl methylphosphonate (**1g**) were treated with $SOCl_2$ under the same conditions, the products were identified as the substrate's hydrochloride salts (**4**) (Equation 2).

TABLE 1 Preparation of Chlorides **2** from Esters **1** and $SOCl_2$ [3]

R-P(O)(OR')₂					
1	*R*	*R'*	**2**	*Bp (°C/mm Hg)*	*Yield (%)*
1a	Me	Me	**2a**	27–28/0.7	68[a]
1b	Me	Et	**2b**	41/1	60[b]
1c	Me	Pr^i	**2c**	36/0.8	62[c]
1d	Et	Et	**2d**	37/0.6	66

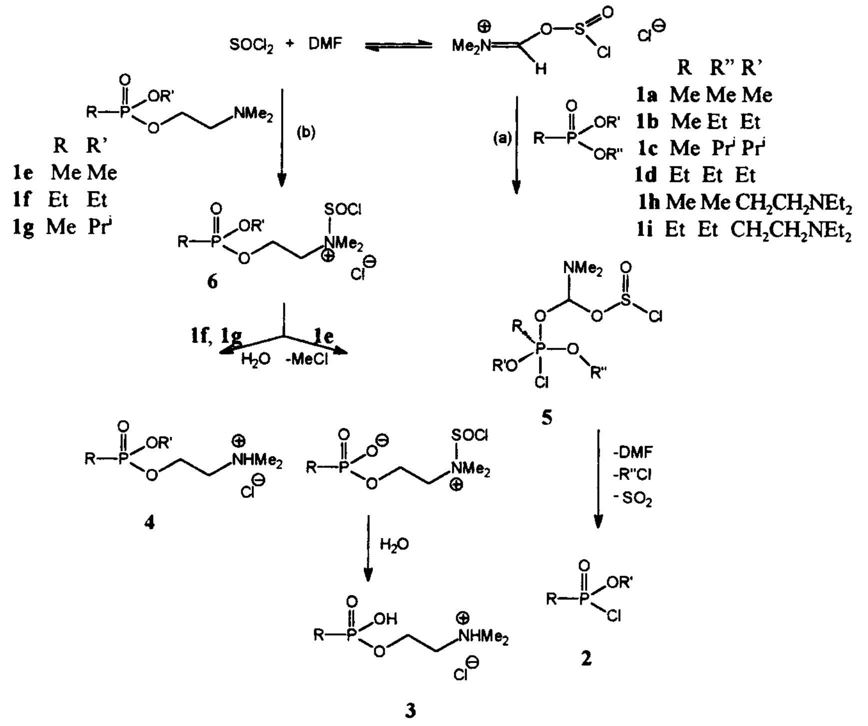
[a] Ref. [3] bp 78–82°C/14 torr; yield 30%.
[b] Ref. [4] bp 83–84°C/23 mm; yield 80%.
[c] Ref. [4] 83°C/22 mm; yield 62%.



(2)

Salts **4** could be converted back to substrates **1f–g** upon treatment with anh. K_2CO_3; they were also prepared independently from **1** and dry HCl. It is clear that the only difference in the behavior of **1f** and **1g** and that of **1e** is that, in the latter, due to the known susceptibility of phosphate methyl esters to nucleophilic displacement [8], the demethylation by the Cl^- ion follows adduct formation. In all three cases, it was the NMe_2 group, not the phosphoryl oxygen, that acted as the reactive center toward $SOCl_2$, preventing the "normal" course of the Maier reaction.

Quite surprisingly, the behavior of two other substrates, methyl (2-diethylamino)ethyl methylphosphonate (**1h**) and ethyl (2-diethylamino)ethyl ethylphosphonate (**1i**), was found to be essentially different from that of the (2-dimethylamino)ethyl derivatives **1e**, **1f**, or **1g**. When **1h** and **1i** were treated with $SOCl_2$/DMF [3], crude products were obtained as pale-yellow oils in high yields. NMR spectroscopic analysis of the freshly prepared products demonstrated their homogeneity (single signal in the ^{31}P NMR spectrum), and they were identified as the desired phosphonomonochloridates (**2h**, **2i**) according to the following criteria: (1) ^{31}P NMR chemical shift values (δ_P 43.3, 49.7) correspond closely to those observed for other phosphonochloridates **2a–2d**; (2) ^{1}H NMR spectra showed the absence of the OMe or OEt group at phosphorus, and the δ_H values of the remaining signals were in agreement with the expected effect of the chlorine atom replacing one of



SCHEME 1

the ester groups; and (3) most importantly, products **2h** and **2i** were, in agreement with our expectations, highly unstable and decomposed spontaneously as neat oils or in solutions. Because of that instability, **2h** and **2i** could not be purified either by distillation or by column chromatography, but the kinetics and the mechanism of their fragmentation could be conveniently studied [5] and compared with the fragmentation of the related phosphonofluoridates [9].

In conclusion, we propose a general mechanism for Maier's reaction of converting phosphonic diesters into their monochloridate derivatives. In the absence of other nucleophilic centers in a substrate, the phosphoryl oxygen reacts with the $SOCl_2 \cdot DMF$ adduct (presented, as suggested by Maier [3], as an iminium salt) yielding a P^V intermediate **5**, which can collapse to the final products (Scheme 1, a). In the case of the presence of a (2-dialkylamino)ethyl substituent, the initial reaction with $SOCl_2$ can take place at the nitrogen [7], leading to an ionic intermediate **6** (Scheme 1, b). For the O-methyl substrates (e.g., **1e**, R′ = Me), nucleophilic demethylation occurs, finally yielding the hydrochloride of the O-demethylated substrate (**3**). For the O-alkyl esters with $R' \neq Me$ (**1f**, **1g**), no effective dealkylation by the Cl^- ion is observed, and the substrate's conjugate acid (**4**) is the only reaction product. As a salt, it precipitates out of the solution, what may prevent its further conversion. Of most interest, however, is that simple substitution of the N,N-dimethyl group for the N,N-diethyl substituent (**1e** → **1h**; **1f** → **1i**) provides enough steric hindrance at nitrogen that the initial reaction with $SOCl_2$ again involves the P=O group; hence, the Maier reaction can proceed in a normal way (Scheme 1, a). It is also interesting to note that, while the OEt group remained intact in the reaction of **1f** (no O-dealkylation by Cl^-), it was removed in the preparation of **2i** from **1i**. This result could be taken as a support of the intramolecular, hence, favored displacement of the R′ group by chloride, but the exact mechanism of the collapse of the intermediate requires further investigation.

EXPERIMENTAL SECTION

Solvents and commercially available substrates were purified by conventional methods immediately before use. NMR spectra were recorded on a Bruker AC300 spectrometer; the chemical shift values are given in ppm relative to $SiMe_4$ (^1H and ^{13}C) as an internal standard and 85% H_3PO_4 (^{31}P) as an external standard. Melting points were determined on a Gallenkamp melting point apparatus and are uncorrected. Elemental analyses were performed at the Chemistry Department, University of Cape Town.

Dialkyl alkylphosphonates **1a–1d** were prepared from the corresponding trialkyl phosphites and haloalkanes according to the procedures given in the literature [10]. The physical data were in full agreement with those reported, and their NMR (^1H, ^{31}P) spectra corresponded well to the expected structures.

TABLE 2 NMR Spectra of **2a–2d** (CDCl$_3$ 30°C); Coupling Constants Given in Hz

R-P(O)(OR')Cl	δ_P	δ_H (*R*)	δ_H (*R'*)
2a, R = R' = Me	42.8	1.95 (d, 17.6, 3H)	3.84 (d, 13.5, 3H)
2b, R = Me; R' = Et	40.7	1.94 (d, 17.5, 3H)	1.37 (t, 7.1, 3H), 4.24 (m, 2H)
2c, R = Me; R' = Pr$_i$	39.2	1.92 (d, 17.6, 3H)	1.38 (dq, 6.2, 4.0, 6H), 4.94 (m, 1H)
2d, R = R' = Et	47.3	1.25 (dt, 24.7, 7.7, 3H), 2.11 (dq, 17.4, 7.6, 2H)	1.36 (t, 7.0, 3H), 4.24 (m, 2H)

Preparation of 2a–2d *[3].* A mixture of 1 (one mol-equiv.), DMF (0.01 mol-equiv.), and freshly distilled SOCl$_2$ (2.5 mol-equiv.) was heated under reflux for 2.5 hours. The excess of SOCl$_2$ was distilled off at the lowest possible temperature, and the products were purified by distillation under reduced pressure (Table 1). All products gave a single signal in the ^{31}P NMR spectra, and their ^{1}H NMR spectra were in full agreement with the expected structures (Table 2).

Preparation of Alkyl (2-Dialkylamino)ethyl Alkylphosphonates 1e–1i. *General Procedure (Modified Procecure Taken from Ref. [9]).* A solution of N,N-dialkylaminoethanol (1 mol-equiv.) and triethylamine (1.1 mol-equiv.) in ether (0.35 mL per mmol) was added dropwise to a stirred solution of alkyl alkylphosphonochloridate 2 (1 mol-equiv.) in ether (1.75 mL per mmol) at −15°C. After addition, the mixture was stirred at −15°C for 1 hour and allowed to warm to room temperature. The precipitate was filtered off, dissolved in chloroform (3.5 mL per mmol), and anh. K$_2$CO$_3$ (1.15 mol-equiv.) was added to the solution. The solution was stirred at room temperature overnight, filtered, and the solvent was removed from the filtrate under reduced pressure. The crude products were purified by bulb-to-bulb distillation.

1e (33%), 60°C/0.5 mm Hg. ^{1}H NMR (CDCl$_3$) δ 1.46 (d, J = 17.4 Hz, 3H), 2.24 (s, 6H), 2.54 (t, J = 5.7 Hz, 2H), 3.69 (d, J = 11.3 Hz, 3H), 4.08 (m, 2H); ^{1}H-coupled ^{13}C NMR δ 10.5 (dq, J = 144.8, 128.4 Hz), 45.6 (q, J = 133.1 Hz), 51.9 (dq, J = 6.3, 147.3 Hz), 59.3 (dt, J = 5.8, 131.7 Hz), 63.1 (dt, J = 15.5, 147.4 Hz); ^{31}P NMR δ 33.1. Anal. calcd for C$_6$H$_{16}$NO$_3$P (181.6): C, 39.78; H, 8.84; N, 7.74. Found: C, 39.50; H, 8.96; N, 7.33.

1f (22%), 75°C/0.3 mm Hg. ^{1}H NMR (CDCl$_3$) δ 1,12 (dt, J = 20.0, 7.7 Hz, 3H), 1.29 (t, J = 7.0 Hz, 3H), 1.73 (dq, J = 18.3, 7.7 Hz, 2H), 2.24 (s, 6H), 2.55 (t, J = 5.9 Hz, 2H), 4.07 (m, 4H); ^{1}H-coupled ^{13}C NMR δ 6.5 (dq, J = 6.4, 129.3 Hz), 16.4 (dq, J = 6.4, 127.1 Hz), 18.8 (dt, J = 143.1, 126.7 Hz), 45.7 (q, J = 133.2 Hz), 59.4 (dt, J = 6.4, 132.8 Hz), 61.6 (dt, J = 6.4, 146.6 Hz), 63.1 (dt, J = 6.4, 146.3 Hz); ^{31}P NMR δ 34.8. Anal. calcd for C$_8$H$_{20}$NO$_3$P (209.3): C, 45.93; H, 9.65; N, 6.70. Found: C, 45.62; H, 10.01; N, 6.62.

1g (36%), 70°C/0.3 mm Hg. ^{1}H NMR (CDCl$_3$) δ 1.28 (d, J = 6.2 Hz, 6H), 1.44 (d, J = 17.5 Hz, 3H), 2.24 (s, 6H), 2.54 (t, J = 5.9 Hz, 2H), 4.05 (m, 2H), 4.66 (m, 1H); ^{1}H-coupled ^{13}C NMR δ 11.9 (dq, J = 144.9, 128.1 Hz), 23.9 (dq, J = 4.1, 126.7 Hz), 45.6 (q, J = 133.2 Hz), 59.2 (dt, J = 6.4, 131.3 Hz), 62.8 (dt, J = 6.3, 146.1 Hz), 70.2 (dd, J = 6.3, 146.3 Hz); ^{31}P NMR δ 30.6. Anal. calcd for C$_8$H$_{20}$NO$_3$P: C, 45.93; H, 9.65; N, 6.70. Found: C, 45.25; H, 9.99; N, 6.66.

1h (6%), 87°C/0.9 mm Hg. ^{1}H NMR (CDCl$_3$) δ 0.99 (t, J = 7.2 Hz, 6H), 1.44 (d, J = 17.5 Hz, 3H), 2.54 (q, J = 7.1 Hz, 4H), 2.68 (t, J = 6.3 Hz, 2H), 3.68 (d, J = 11.1 Hz, 3H), 4.03 (m, 2H); ^{1}H-coupled ^{13}C NMR δ 10.5 (dq, J = 144.6, 128.5 Hz), 11.6 (q, J = 125.4 Hz), 47.5 (t, J = 132.6 Hz), 52.0 (dq, J = 6.3, 144.2 Hz), 52.8 (dt, J = 6.2, 134.6 Hz), 63.6 (dt, J = 6.4, 147.2 Hz); ^{31}P NMR δ 32.8. Anal. calcd for C$_8$H$_{20}$NO$_3$P: C, 45.93; H, 9.65; N, 6.70. Found: C, 45.50; H, 10.15; N, 6.25.

1i (39%), purified by precipitation with dry HCl, filtration, treatment of the precipitate with aq. K$_2$CO$_3$ and extraction with CHCl$_3$. Colorless oil. ^{1}H NMR (CDCl$_3$) δ 1.00 (t, J = 7.1 Hz, 6H), 1.12 (dt, J = 20.0, 7.7 Hz, 3H), 1.28 (t, J = 7.1 Hz, 3H), 1.73 (dq, J = 18.3, 7.7 Hz, 2H), 2.56 (q, J = 7.1 Hz, 4H), 2.70 (t, J = 6.4 Hz, 2H), 4.07 (m, 4H); ^{1}H-coupled ^{13}C NMR δ 6.3 (q, J = 130.0 Hz), 11.6 (q, J = 125.4 Hz), 16.2 (dq, J = 5.9, 126.9 Hz), 18.6 (dt, J = 142.7, 126.8 Hz), 47.4 (t, J = 132.8 Hz), 52.7 (dt, J = 6.3, 133.0 Hz), 61.3 (dt, J = 6.4, 148.5 Hz), 63.3 (dt, J = 6.5, 149.7 Hz); ^{31}P NMR δ 34.6. Anal. calcd for C$_{10}$H$_{24}$NO$_3$P: C, 50.68; H, 10.21; N, 5.91. Found: C, 50.25; H, 10.38; N, 5.75.

Reactions of 1e–1i *with SOCl$_2$/DMF. General Procedure.* Each alkyl (2-dialkylamino)ethyl alkylphosphonate 1e–1i was treated with SOCl$_2$/DMF as described previously for the preparation of 2a–2d. After the removal of the excess of SOCl$_2$, the following results were obtained.

From 1e. Yellow precipitate was filtered off, dissolved in a minimum volume of CHCl$_3$, and precipitated again with a fivefold volume of ether. White solid (58%), mp 119°C, was identified as the hydrochloride of (2-dimethylamino)ethyl methylphosphonate (**3**). ^{1}H NMR (D_2O) δ 1.35 (d, J = 16.9 Hz, 3H), 2.86 (s, 6H), 3.35 (t, J = 5.0 Hz, 2H), 4.13 (m, 2H); ^{1}H-coupled ^{13}C NMR δ 13.3 (dq, J = 137.3, 127.6 Hz), 45.5 (q, J = 143.9 Hz), 60.0 (dt, J = 7.6, 143.2 Hz), 60.8 (dt, J = 4.6, 148.9 Hz); ^{31}P NMR δ 30.6. Anal. calcd for $C_5H_{15}ClNO_3P$ (203.6): C, 29.48; H, 6.87; N, 7.42. Found: C, 27.96; H, 6.78; N, 7.78.

The same product (mp, ^{1}H, ^{13}C, ^{31}P NMR spectra) was obtained in the following manner. **1e** (0.211 g, 1.17 mmol) was dissolved in dry ether (50 mL), and dry HCl was bubbled through the solution at room temperature for 45 minutes. The solution was evaporated under reduced pressure, and the remaining colorless oil was identified as the salt of **1e** (**1e** · **HCl**). ^{1}H NMR (D_2O) δ 1.52 (d, J = 17.6 Hz, 3H), 2.88 (s, 6H), 3.38 (t, J = 5.0 Hz, 2H), 3.70 (d, J = 11.2 Hz, 3H), 4.44 (m, 2H); ^{31}P NMR δ 34.0.

The foregoing product (0.186 g, 0.85 mmol) was dissolved in $SOCl_2$ (0.51 g, 4.24 mmol), and the solution was heated under reflux for 30 minutes. The excess of $SOCl_2$ was removed under reduced pressure, and the white precipitate (0.138 g, 79%) was identified as salt **3** described earlier.

From **1f**. A pale-yellow, hygroscopic oil (69%) was identified as the hydrochloride salt of the substrate (**1f** · **HCl**). ^{1}H NMR (D_2O) δ 1.16 (dt, J = 20.7, 7.7 Hz, 3H), 1.33 (t, J = 7.0 Hz, 3H), 1.83 (dq, J = 18.7, 7.7 Hz, 2H), 2.91 (s, 6H), 3.39 (m, 2H), 4.14 (m, 2H), 4.51 (m, 2H); ^{31}P NMR δ 36.5. When a chloroform solution of the foregoing product was treated with anh. K_2CO_3 (1.1 mol-equiv.), the mixture filtered, evaporated, and examined by NMR (^{1}H, ^{13}C, ^{31}P) spectroscopy, it was shown that the starting material **1f** was recovered. **1f** · **HCl** was also obtained as a hygroscopic semisolid by passing dry HCl through a solution of **1f** in ether. The NMR (^{1}H and ^{31}P) spectra of this product were identical to those of **1f** · **HCl** described earlier. Anal. calcd for $C_8H_{21}ClNO_3P \cdot H_2O$: C, 36.44; H, 8.78; N, 5.31. Found: C, 36.00; H, 8.98; N, 5.15.

From **1g**. A white hygroscopic solid (35%) was obtained by precipitation with ether and identified as the hydrochloride salt of the substrate (**1g** · **HCl**). ^{1}H NMR (D_2O) δ 1.30 (dd, J = 2.5, 6.2 Hz, 6H), 1.52 (d, J = 17.5 Hz, 3H), 2.88 (s, 6H), 3.36 (t, J = 4.9 Hz, 2H), 4.46 (m, 2H), 4.67 (m, 1H); ^{31}P NMR δ 31.4. Treatment of the product with anh. K_2CO_3 permitted the recovery of **1g** (88%) that showed NMR (^{1}H and ^{31}P) spectra identical to those of the starting material. **1g** · **HCl** was also obtained from **1g** and dry HCl; a white, hygroscopic solid with ^{1}H and ^{31}P NMR spectra (D_2O) identical to those described earlier.

From **1h**. A pale-yellow oil (87%) identified as (2-diethylamino)ethyl methylphosphonochloridate (**2h**). ^{1}H NMR ($CDCl_3$) δ 1.41 (t, J = 7.3 Hz, 6H), 2.10 (d, J = 17.5 Hz, 3H), 3.21 (m, 4H), 3.41 (m, 2H), 4.67 (m, 2H); ^{31}P NMR δ 43.3. When a solution of **2h** in $CDCl_3$ was kept at room temperature and examined periodically by NMR spectroscopy, ^{1}H NMR spectra revealed slow formation of diethyl(2-chloroethyl)amine; δ 1.42 (t, J = 7.3 Hz, 6H), 3.34 (t, J = 6.8 Hz, 2H), 4.02 (t, J = 6.8 Hz, 2H). The product was identified by the addition of the authentic material generated from the commercially available hydrochloride salt. The ^{31}P NMR spectrum showed formation of a large number of signals of unidentified products (see Ref. [5]).

From **1i**. A pale-yellow oil (86%) identified as (2-diethylamino)ethyl ethylphosphonochloridate (**2i**). ^{1}H NMR ($CDCl_3$) δ 1.27 (dt, J = 25.4, 7.7 Hz, 3H), 1.40 (t, J = 7.3 Hz, 6H), 2.25 (dq, J = 17.2, 7.6 Hz, 2H), 3.21 (m, 4H), 3.41 (m, 2H), 4.66 (m, 2H); ^{31}P NMR δ 49.7. Further spectroscopic (^{1}H and ^{31}P NMR) examination of the $CDCl_3$ solution of **2i** demonstrated slow formation of diethyl(2-chloroethyl)amine, the same product as observed for **2h**.

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