Evidence for Cyclic Azaphosphiridine Oxide Intermediates in the Methoxide-induced Rearrangements of *N*-Alkyl α-Chlorophosphonamidates: Formation of Phosphoramidates as well as α-Aminophosphonates [1]

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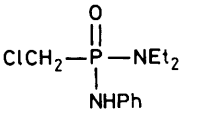
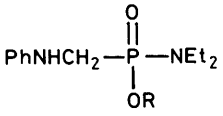
The *N*-t-butyl α-chlorophosphonamidates RCHClP(O)(NHBu^t)OMe (R = H, Me, or Ph) react with benzyltrimethylammonium methoxide in tetrahydrofuran–methanol to give two types of rearrangement product, the α-aminophosphonates Bu^{t}NHCHRP(O)(OMe)$_2$ and the phosphoramidates Bu^t(RCH$_2$)N-P(O)(OMe)$_2$. For the phosphoramidates it seems necessary to postulate the formation of a cyclic azaphosphiridine oxide intermediate, and its subsequent ring-opening, by nucleophilic attack of methoxide at phosphorus, with cleavage of the P–C bond. The α-aminophosphonates are probably also derived from the azaphosphiridine oxide, by cleavage of the P–N bond. The observation that the proportion of the phosphoramidate (P–C cleavage) increases as R changes from Me to H to Ph accords with this picture, as does the apparent lack of any P–C bond cleavage in the rearrangement of Me$_2$CClP(O)(NHR')OMe (R' = Me or Bu^t).

When the α-chlorophosphonic diamide (**1**) is heated with RONa–ROH in dimethylformamide the phenylamino group migrates from phosphorus to the α-carbon atom and the α-anilino compound (**2**; R = Me, Et, or Ph) is obtained in good yield (50—80%).[2] Comparable behaviour has recently been observed with *N*-phenyl α-chlorophosphonamidates, including the more highly alkylated substrates (**3**; R = H) and (**3**; R = Me),[3] suggesting that this type of rearrangement has considerable generality and synthetic potential.



(**1**)



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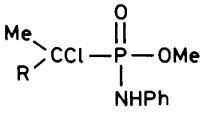

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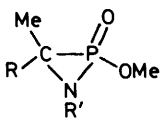


(**4**)

We have now examined the behaviour of some related α-chlorophosphonamidates in which the *N*-phenyl group is replaced by *N*-alkyl. We hoped not only to extend the scope of the rearrangement but more particularly to find some firm evidence for azaphosphiridine oxide intermediates such as (**4**); hitherto such evidence has been largely circumstantial.[2,3]

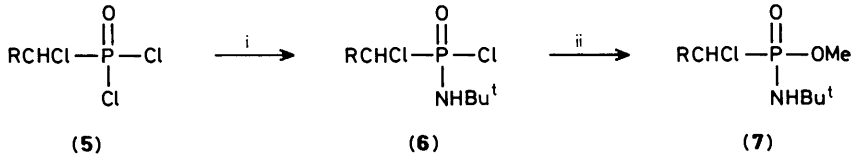
Results and Discussion

The *N*-t-butyl α-chlorophosphonamidates (**7**; R = H, Me, or Ph) were prepared from the appropriate phosphonic dichlorides (**5**) by the sequence of reactions shown in Scheme 1. This approach had the advantage that the intermediate phosphonamidic chlorides (**6**) could be purified by crystallisation before the methoxy group was introduced.

In the case of the more hindered phosphonic dichloride (**8**) the reaction with t-butylamine occurred only under rather forcing conditions and then did not give a useful amount of the phosphonamidic chloride: the phosphonic diamide (**9**) was much the major product, together with unchanged starting material. This is doubtless a consequence of the ability of the phosphonamidic chloride, but not the phosphonic dichloride, to react with Bu^{t}NH$_2$ by a dissociative elimination–addition substitution mechanism (monomeric metaphosphonimidate intermediate),[4] thereby avoiding the steric congestion inherent in the usual S_N2(P) mechanism.

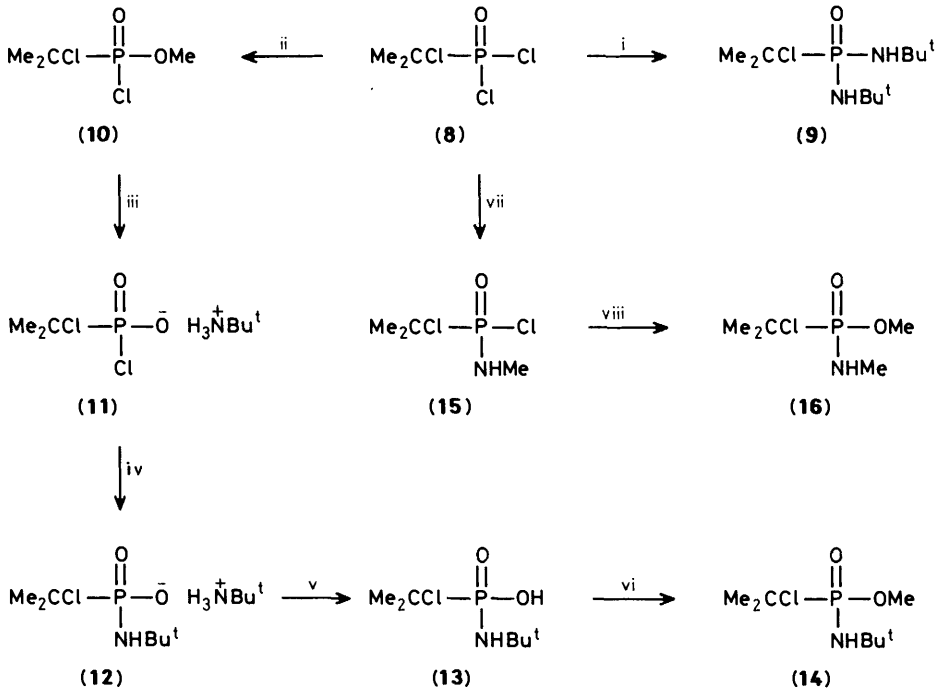
Selective replacement of just one of the chlorines in the dichloride (**8**) was possible with NaOMe,[3] but unfortunately the resulting methyl phosphonochloridate (**10**) did not give the required methyl phosphonamidate on treatment with Bu^{t}NH$_2$. Instead, the salt (**11**) was formed by demethylation, and the P–Cl bond remained intact. It is now known that Bu^{t}NH$_2$ is an effective reagent for dealkylating the methyl esters of P^V acids;[5] in the case of (**10**) this demethylation, by S_N2 attack at carbon, evidently occurs more readily than displacement of chlorine by attack of the nucleophile at the sterically congested P atom. When the salt (**11**) was heated in Bu^{t}NH$_2$ the P–Cl bond did react, presumably by an elimination–addition mechanism (monomeric metaphosphonate intermediate), and the new salt (**12**) was formed (together with other products). Acidification gave the phosphonamidic acid (**13**) which was converted into the required phosphonamidate (**14**) by treatment with diazomethane.

In contrast to Bu^{t}NH$_2$, sterically undemanding MeNH$_2$ reacted quite readily with the phosphonic dichloride (**8**); the



(**5**) (**6**) (**7**)

Scheme 1. *Reagents:* i, Bu^{t}NH$_2$; ii, NaOMe

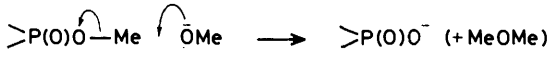


Scheme 2. *Reagents:* i, Bu^tNH_2; ii, NaOMe; iii, Bu^tNH_2; iv, Heat, Bu^tNH_2; v, HCl; vi, CH_2N_2; vii, $MeNH_2$; viii, NaOMe

phosphonamidic chloride (**15**) was obtained in high yield, and was converted into the *N*-methyl phosphonamidate (**16**).*

All the phosphonamidic chlorides and methyl phosphonamidates were crystalline solids, in spite of the fact that those derived from (**5**; R = Me) and (**5**; R = Ph) were obtained, as expected, as mixtures of diastereoisomers. The diastereoisomers were easily distinguished by ^1H and ^{31}P n.m.r. spectroscopy, but recrystallisation did not generally afford useful separation, and the diastereoisomer mixtures were employed in subsequent reactions.

The α-chloroethylphosphonamidate (**7**; R = Me) reacted rather slowly when heated with 1.8M NaOMe in MeOH ($t_{\frac{1}{2}}$ *ca.* 2.7 h at 60 °C). Monitoring of the reaction by g.l.c. showed the formation of two products, in unequal yield (ratio *ca.* 8:1), but it also revealed that the major product suffered extensive degradation as the reaction proceeded. Since the lost product was restored when the reaction mixture was acidified and treated with diazomethane, it seems clear that the degradation was, in fact, nothing more than demethylation:

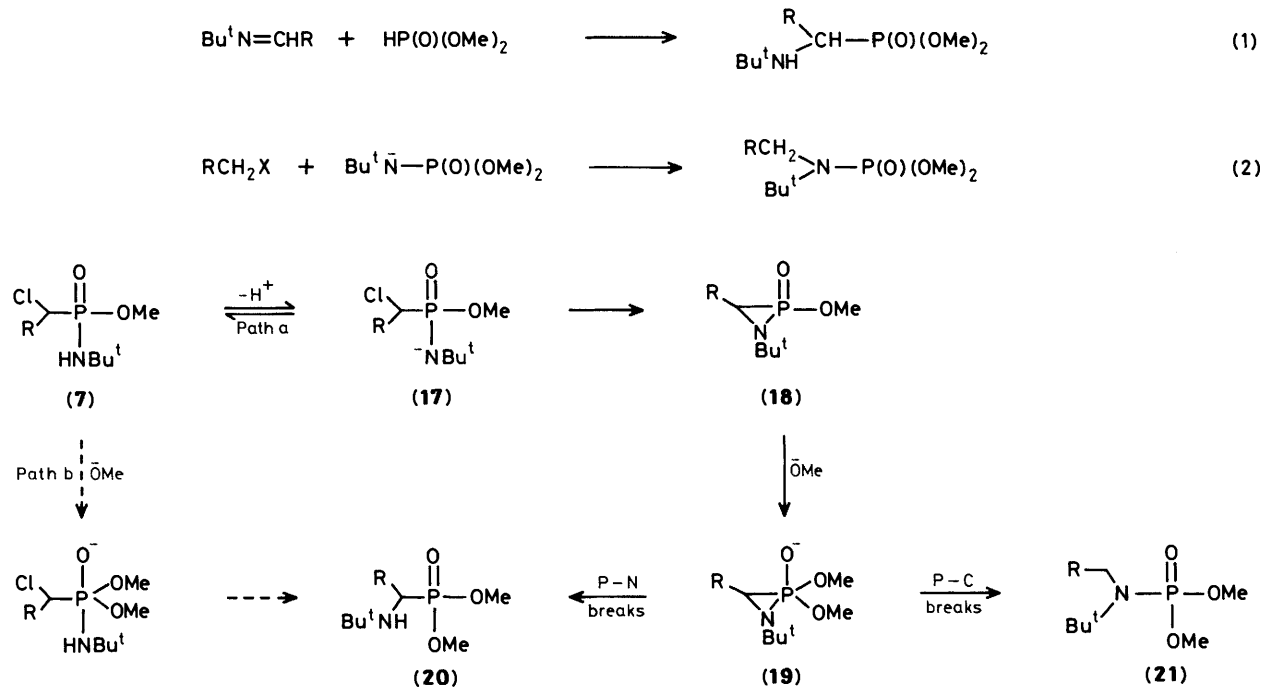


Reaction occurred much more readily with benzyltrimethylammonium methoxide (QOMe) (2 mol equiv.) in THF–MeOH (*ca.* 7:1, v/v), allowing the use of both a smaller concentration of base (0.26M initially) and a lower temperature (50 °C; ≥95% complete in 1.25 h). Only a small difference in the reactivity of the two diastereoisomers of the substrate (δ_P 25.0 and 25.4) was apparent (δ_P 25.0 slightly greater), and under these milder conditions the major product suffered relatively little demethylation. The two products (δ_P 30.3 and 12.4), formed in a ratio of *ca.* 9:1 (^1H and ^{31}P n.m.r.), were separated by partition between dichloromethane and aqueous HCl. The major, acid-soluble product (δ_P 30.3) had spectroscopic properties in accord with the α-aminophosphonate structure (**20**; R = Me) and was, therefore, the product expected by analogy with the rearrangement of the corresponding *N*-phenyl substrate (**3**; R = H).[3] The minor, neutral product (δ_P 12.4) had the same molecular formula and also contained two *P*-methoxy groups (δ_H 3.64, 6 H, d, J_{PH} 11 Hz) and an *N*-t-butyl group (δ_H 1.27, 9 H, s). However, the methoxy groups were now equivalent rather than diastereotopic, there was no N–H bond (i.r., ^1H n.m.r.), and most significantly, the ^1H n.m.r. spectrum revealed an *N*-ethyl group with three-bond coupling of the methylene protons to phosphorus (δ_H 3.11, 2 H, dq, J_{PH} 14, J_{HH} 7 Hz). These features were indicative of the phosphoramidate structure (**21**; R = Me). The identities of both products were established beyond doubt by comparison with samples of the same compounds prepared by more conventional routes, namely addition of dimethyl phosphite to the imine [equation (1); R = Me][6] and alkylation of the sodium salt of dimethyl *N*-t-butylphosphoramidate [equation (2); R = Me].[7]

The α-chloromethyl compound (**7**; R = H) also gave two products (δ_P 29.3 and 12.3) with QOMe in THF–MeOH, but now their ratio was 1:1.6 and the expected α-aminophosphonate (**20**; R = H) was the lesser of the two. The major product (δ_P 12.3) was the phosphoramidate (**21**; R = H), identical with an authentic sample prepared as before [equation (2); R = H].

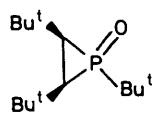
The phosphoramidate products obtained in the reactions of (**7**; R = H) and (**7**; R = Me) are of great mechanistic significance. Whereas the α-aminophosphonates might reasonably be formed by either of the pathways shown in Scheme 3, depending on whether methoxide acts initially as a base (path a) or a nucleophile (path b), only path a can reasonably account for the formation of the phosphoramidates. The key feature of path a is the cyclic azaphosphiridine oxide intermediate (**18**),

* It is still the case that only a few *N*-alkylphosphonamidic chlorides RP(O)(Cl)NHR′ (R = alkyl or aryl, R′ = alkyl) have been successfully prepared, and practically all those that have seem to owe their stability to the presence of a bulky *N*-alkyl group (R′ = Bu^t) (ref. 4). The preparation and isolation of the *N*-methylphosphonamidic chloride (**15**) is, therefore, of considerable interest; presumably the bulky Me_2CCl group on phosphorus is responsible for the stability in this case [see S. Freeman and M. J. P. Harger, *J. Chem. Soc., Perkin Trans. 1*, 1987, 1399 (especially footnote on p. 1400)].

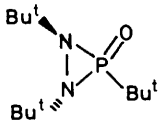


Scheme 3.

the phosphorus analogue of an α-lactam.[8] Three-membered rings containing a P=O group have attracted considerable attention in recent years,[9] both as short-lived reaction intermediates[10] and, in special cases, as isolable compounds, *e.g.* (**22**)[11] and (**23**).[12] However, it seems that azaphosphiridine oxides have never been isolated, nor previously has there even been firm evidence for their occurrence as reaction intermediates. Certainly the P=O group in a three-membered ring is expected to be highly reactive towards a nucleophile like methoxide, especially if a five-co-ordinate intermediate [*e.g.* (**19**)] is formed.[13]

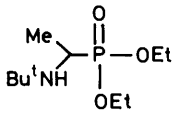


(**22**)

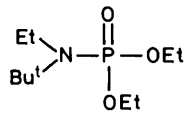


(**23**)

Granted that the phosphoramidate products are formed by way of azaphosphiridine oxide intermediates (Scheme 3, path a), the probability must be that the α-aminophosphonates are as well. Nonetheless, it remains a possibility that the aminophosphonates are produced independently, by the alternative pathway (path b). With this in mind, we examined the rearrangement of the *O*-ethyl analogue of the substrate (**7**; R = Me) with NaOEt in EtOH. Compared with the reaction of the *O*-methyl compound in MeOH–NaOMe, nucleophilic attack at phosphorus (path b) should be discouraged by steric factors in both the reagent and the substrate,[14] whereas elimination of HCl (path a) should be encouraged by the enhanced basicity of the reaction medium.[15] Individually these effects would probably be small, but together their influence could be substantial. Although the α-aminophosphonate/phosphoramidate product ratio (**24**)/(**25**) (*ca.* 5:1) was somewhat smaller than for the *O*-methyl compound in MeOH (*ca.* 8:1), the change was certainly not as great as would be expected if path b were the only, or even the principal, route to the aminophosphonate. There may be some contribution from this pathway, but it seems more reasonable to suppose that the α-aminophosphonate, like the phosphoramidate, is formed entirely *via* the azaphosphiridine oxide intermediate.

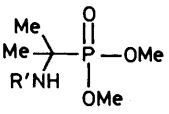


(**24**)

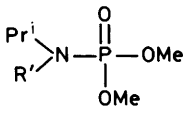


(**25**)

The competition between P–N and P–C bond cleavage in the ring-opening of the azaphosphiridine oxide (Scheme 3) will, of course, depend on the relative abilities of the N and C atoms to support the developing negative charge. In our earlier experiments the presence of a phenyl group on the amide N atom will have assisted P–N cleavage, so it is not surprising that we were unable to detect the phosphoramidates that would have resulted from P–C cleavage.[3] In the present experiments the substituent on the amide N atom is t-butyl, so P–C cleavage should be much better able to compete effectively. It is therefore not unreasonable that some phosphoramidate should now be formed, or that the contribution of P–C cleavage should diminish in going from the unalkylated substrate (**7**; R = H) to one with a methyl group on the α-carbon (**7**; R = Me). For a substrate with two methyl groups on the α-carbon atom, P–C cleavage should be still less important. In the event the substrate (**14**) gave the expected α-aminophosphonate (**26**; R′ = Bu^t) (*ca.* 70% by ^{31}P n.m.r.; 49% isolated) with QOMe in THF–MeOH, but several minor products were also formed.



(**26**)



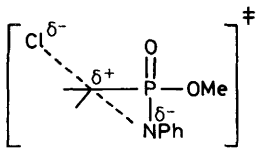
(**27**)

None of these had a ^{31}P chemical shift in the region expected (δ_P 12—14) for the phosphoramidate (**27**; R′ = Bu^t) that would result from P–C cleavage, but since no authentic sample was

available it was impossible to be sure. In the case of the corresponding *N*-methyl substrate (**16**) an authentic sample of the phosphoramidate (**27**; R′ = Me) could be prepared [MeI + $Pr^iNP(O)(OMe)_2$]. This substrate reacted more cleanly, to give the α-aminophosphonate (**26**; R′ = Me), and although a minor product (δ_P 4.0) (*ca.* 10%) was observed, it was not the phosphoramidate (**27**; R′ = Me); control experiments with the authentic sample of (**27**; R′ = Me) showed that neither it (δ_P 12.4) nor its degradation product (δ_P 8.1) was present in the reaction mixture.

In contrast to methyl, a phenyl group on the α-carbon would be expected to stabilise negative charge and so encourage P–C cleavage in the breakdown of the azaphosphiridine oxide. This proved to be the case, to the extent that the benzylic substrate (**7**; R = Ph) gave the phosphoramidate (**21**; R = Ph) as the only substantial product (^{31}P n.m.r., g.l.c.; 96% isolated) with QOMe in THF–MeOH. This substrate was markedly more reactive than any of the others, so that even at a substantially lower temperature (25 °C as opposed to 50 °C) reaction was complete in a rather shorter time. It was possible, with the aid of an authentic sample [equation (1); R = Ph], to detect a trace of the α-aminophosphonate (**20**; R = Ph) but its yield was only *ca.* 1%. Taken with our earlier results,[3] it can now be seen that even quite modest changes to the structure of the α-chlorophosphonamidate can change dramatically the outcome of its methoxide-induced rearrangement. It is interesting to note that when the rearrangement of the benzylic substrate (**7**; R = Ph) was carried out in MeOH with NaOMe as base (T = 50 °C) P–C cleavage was less dominant, the product ratio being 88:12. The reason for this change is not known, but it may be that the benzylic C atom gains less benefit from the presence of the phenyl group because the developing negative charge (on C or N) is stabilised better with MeOH as solvent and Na^+ as counter ion. Better stabilisation of an anion—the conjugate base (**17**) of the substrate—may also be responsible, in part at least, for all the rearrangements being markedly slower with NaOMe in MeOH than with QOMe in THF–MeOH.

The benzylic substrate apart, the rates at which the various *N*-t-butyl α-chlorophosphonamidates underwent rearrangement with QOMe in THF–MeOH differed little.* This is in sharp contrast to the situation with the *N*-phenyl substrates studied earlier; there the rate of rearrangement (with NaOMe in MeOH) increased by a factor of 50—60 each time a hydrogen on the α-carbon atom was replaced by a methyl group, possibly because of some S_N1 character in the transition state (**28**) for cyclisation.[3] With the *N*-alkyl substrates the charge on the N atom of the conjugate base will be more localised; a consequence may be that N–C bond making is further advanced in the transition state (**29**), and the S_N1 character is correspondingly less. Of course, it might simply be that the bulk of the alkyl substituent (Bu^t) on the N atom gives rise to adverse steric interactions with the methyl groups on the α-carbon in the transition state, cancelling out almost all of the advantage they would otherwise confer. This seems unlikely, however, since the rate of rearrangement of the most alkylated (and sterically congested) substrate (**14**) increased only 2—3 fold when the t-butyl group on the nitrogen atom was replaced by a much less bulky methyl group.



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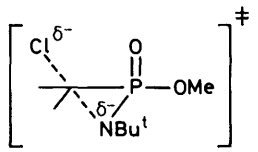

(**29**)

Experimental

Instrumentation was as previously described.[3] Tetrahydrofuran (THF) was always redistilled immediately prior to use. Methanol and ethanol were purified by distillation from their magnesium salts. Light petroleum refers to the fraction b.p. 60—80 °C unless otherwise indicated.

α-Chlorophosphonic Dichlorides.—1-Chloro-1-phenylmethylphosphonic dichloride (**5**; R = Ph) (55%) was prepared by heating benzaldehyde and phosphorus trichloride[16] at 195—200 °C (oven temp.) for 7.5 h; it distilled at 109 °C at 0.3 mmHg (lit.,[17] 132 °C at 2 mmHg) and solidified on cooling (m.p. *ca.* 55 °C); $\delta_P(CDCl_3)$ 40.4; $\delta_H(CDCl_3)$ 7.6—7.2 (5 H, m) and 5.34 (1 H, d, J_{PH} 6 Hz). The phosphonic dichlorides (**5**; R = H), (**5**; R = Me), and (**8**) were prepared as before.[3]

α-Chlorophosphonamidates.—The α-chlorophosphonic dichloride was treated with t-butylamine (or methylamine) (2 mol equiv.) to give the α-chlorophosphonamidic chloride which was converted into the α-chlorophosphonamidate using a slight excess of sodium methoxide (or sodium ethoxide). The following is respresentative of the procedure.

A solution of chloromethylphosphonic dichloride (2.00 g, 12.0 mmol) in dichloromethane (12 ml) was stirred at 0 °C while a solution of t-butylamine (1.75 g, 24.0 mmol) in dichloromethane (6 ml) was added dropwise during 0.3 h. The mixture was allowed to warm to room temperature and was then boiled gently under reflux for 0.5 h (or until ^{31}P n.m.r. spectroscopy showed reaction to be complete). The solid (Bu^tNH_3Cl) was filtered off and washed with dichloromethane and the filtrate was evaporated to dryness. Crystallisation from ether afforded N-*t-butyl*-P-(*chloromethyl*)*phosphonamidic chloride* (**6**; R = H) (2.01 g, 83%), m.p. 101—104 °C; *m/z* 188, 190, 192 (M^+ − Me, 100%) (M^+ not observed); $\nu_{max.}$(Nujol) 3 210 cm^{-1} (NH); $\delta_P(CDCl_3)$ 30.9; $\delta_H(CDCl_3)$ 3.72 (2 H, d, J_{PH} 9 Hz), 3.3 (br, NH), and 1.38 (9 H, s) (satisfactory elemental analysis could not be obtained). The phosphonamidic chloride (1.74 g, 8.5 mmol) was dissolved in methanol (15 ml) and the solution was stirred at 0 °C while 1.0M methanolic sodium methoxide (9.5 mmol) was added dropwise. After a further 0.5 h at room temperature the excess of methoxide was neutralised with solid ammonium chloride. Volatile material was evaporated and the residue was partitioned between chloroform and water. The organic layer was dried (Na_2SO_4) and concentrated. Crystallisation from light petroleum (b.p. 40—60 °C) afforded *methyl* N-*t-butyl*-P-(*chloromethyl*)*phosphonamidate* (**7**; R = H) (1.45 g, 86%), m.p. 64—65 °C; *m/z* 184, 186 (M^+ − Me, 100%); $\nu_{max.}$(Nujol) 3 230 cm^{-1} (NH); $\delta_P(CDCl_3)$ 23.2; $\delta_H(CDCl_3)$ 3.69 (3 H, d, J_{PH} 11 Hz), 3.50 (1 H, d, J_{PH} 10 Hz), 3.48 (1 H, d, J_{PH} 9 Hz), 2.75 (br, NH), and 1.32 (9 H, s) (Found: C, 36.1; H, 7.6; N, 6.9; Cl, 17.8. $C_6H_{15}ClNO_2P$ requires C, 36.1; H, 7.6; N, 7.0; Cl, 17.8%).

The following compounds were similarly prepared. N-*t-Butyl*-P-(1-*chloroethyl*)*phosphonamidic chloride* (**6**; R = Me) (61%), mixture of diastereoisomers, m.p. 117—120 °C (from ether); $\delta_P(CDCl_3)$ 37.0 and 38.5; $\delta_H(CCl_4)$ 4.20 (1 H, dq, $J_{PH} \sim J_{HH} \sim 7$ Hz; some doubling of lines), 3.6 (br, NH), 1.84 and 1.83 (total 3 H; both dd, J_{PH} 19, J_{HH} 7 Hz), and 1.46 (9 H, s); *m/z* 217, 219, 221 (M^+, <1%) and 202, 204, 206 (M^+ − Me, 100); $\nu_{max.}$(Nujol) 3 180 cm^{-1} (NH) (Found: C, 32.9; H, 6.6; N, 6.35. $C_6H_{14}Cl_2NOP$ requires C, 33.05; H, 6.5; N, 6.4%).

Methyl N-*t-butyl*-P-(1-*chloroethyl*)*phosphonamidate* (**7**; R = Me) (89%), mixture of diastereoisomers, m.p. 85—86 °C (from

* For two of the substrates the rate of rearrangement was measured more accurately using NaOMe in MeOH. With 1.8M NaOMe at 60 °C the pseudo-first-order rate constants for (**7**; R = H) and (**7**; R = Me) were 4.8 × 10^{-5} and 7.1 × 10^{-5} s^{-1} respectively.

light petroleum); $\delta_P(CHCl_3)$ 25.5 and 26.5; $\delta_H(CDCl_3)$ 3.87 (1 H, dq, $J_{HH} \sim J_{PH} \sim 7$ Hz), 3.70 and 3.68 (total 3 H; both d, J_{PH} 11 Hz), 2.68 (br, NH), 1.66 (3 H, dd, J_{PH} 16, J_{HH} 7 Hz), and 1.33 (9 H, s); *m/z* 198, 200 (M^+ − Me, 100%); $\nu_{max.}$(Nujol) 3 200 cm^{-1} (NH) (Found: C, 39.2; H, 7.8; N, 6.3. $C_7H_{17}ClNO_2P$ requires C, 39.35; H, 8.0; N, 6.6%).

Ethyl N-*t-butyl*-P-(1-*chloroethyl*)*phosphonamidate* (49%), purified by chromatography, mixture of diastereoisomers, m.p. 104—107 °C; $\delta_P(CH_2Cl_2)$ 23.6 and 24.2; $\delta_H(CDCl_3)$ 4.10 (1 H, m), 3.88 (2 H, dq, $J_{PH} \sim J_{HH} \sim 7$ Hz), 2.65 (br, NH), 1.68 (3 H, dd, J_{PH} 16, J_{HH} 7 Hz), 1.32 (9 H, s), and 1.30 (3 H, t, J_{HH} 7 Hz); *m/z* 227, 229 (M^+, <1%) and 212, 214 (M^+ − Me, 100%); $\nu_{max.}$(Nujol) 3 200 cm^{-1} (NH) (Found: C, 42.1; H, 8.45; N, 6.0. $C_8H_{19}ClNO_2P$ requires C, 42.2; H, 8.4; N, 6.15%).

N-*Methyl*-P-(1-*chloro*-1-*methylethyl*)*phosphonamidic chloride* (**15**) (96%), m.p. 91—93 °C (from ether–light petroleum); $\delta_P(CDCl_3)$ 48.8; $\delta_H(CDCl_3)$ 3.6 (br, NH), 2.82 (3 H, dd, J_{PH} 14, J_{HH} 6 Hz), and 1.83 (6 H, d, J_{PH} 17 Hz); *m/z* 189, 191, 193 (M^+, 5%); $\nu_{max.}$(Nujol) 3 210 cm^{-1} (NH) (Found: C, 25.4; H, 5.1; N, 7.5. $C_4H_{10}Cl_2NOP$ requires C, 25.3; H, 5.3; N, 7.4%). In this preparation the solvent was ether, more dilute solutions of the reactants were used, and heating was avoided.

Methyl N-*methyl*-P-(1-*chloro*-1-*methylethyl*)*phosphonamidate* (**16**) (95%), m.p. 71—73 °C (from ether–light petroleum); $\delta_P(CDCl_3)$ 30.9; $\delta_H(CDCl_3)$ 3.70 (3 H, d, J_{PH} 10 Hz), 2.73 (3 H, br d, J_{PH} 11 Hz), 2.65 (br, NH), and 1.71 (6 H, d, J_{PH} 15 Hz); *m/z* 185, 187 (M^+, 6%), and 108 (M^+ − Me_2CCl, 100); $\nu_{max.}$(Nujol) 3 220 cm^{-1} (NH) (Found: C, 32.4; H, 7.0; N, 7.5. $C_5H_{13}ClNO_2P$ requires C, 32.4; H, 7.1; N, 7.55%).

N-*t-Butyl*-P-(1-*chloro*-1-*phenylmethyl*)*phosphonamidic chloride* (**6**; R = Ph) (58%), mixture of diastereoisomers, m.p. 175—177 °C (softens at 172 °C) (from dichloromethane–light petroleum); $\delta_P(CH_2Cl_2)$ 31.9 and 32.5; $\delta_H(CDCl_3)$ 7.6—7.2 (5 H, m), 5.08 and 5.02 (total 1 H; both d, J_{PH} 10 Hz), 3.3 (1 H, br d, J_{PH} 10 Hz, NH), and 1.34 and 1.31 (total 9 H; both s); *m/z* 279, 281, 283 (M^+, 1%), 264, 266, 268 (M^+ − Me, 80), and 125, 127 ($PhCHCl^+$, 100); $\nu_{max.}$(Nujol) 3 210 cm^{-1} (NH) (Found: C, 46.9; H, 5.9; N, 5.3. $C_{11}H_{16}Cl_2NOP$ requires C, 47.2; H, 5.8; N, 5.0%). The reaction time was extended to 6 h at room temperature in this case. The phosphonamidic chloride was only sparingly soluble in dichloromethane, and although the solid precipitated during the reaction was extracted several times, not all the product was recovered.

Methyl N-*t-butyl*-P-(1-*chloro*-1-*phenylmethyl*)*phosphonamidate* (**7**; R = Ph) (83%), mixture of diastereoisomers, m.p. 148—149.5 °C (from dichloromethane–light petroleum); $\delta_P(CHCl_3)$ 21.6 and 22.0; $\delta_H(CDCl_3)$ 7.55—7.15 (5 H, m), 4.82 (1 H, d, J_{PH} 13 Hz), 3.57 and 3.55 (total 3 H; both d, J_{PH} 11 Hz), 2.55 (br, NH), and 1.25 and 1.20 (total 9 H; both s); *m/z* 275, 277 (M^+, <1%), 260, 262 (M^+ − Me, 65), and 150 (M^+ − PhCHCl, 100); $\nu_{max.}$(Nujol) 3 275 and 3 220 cm^{-1} (NH) (Found: C, 52.3; H, 6.9; N, 5.0. $C_{12}H_{19}ClNO_2P$ requires C, 52.3; H, 6.95; N, 5.1%).

t-*Butylammonium* 1-*Chloro*-1-*methylethylphosphonochloridate* (**11**).—Methyl 1-chloro-1-methylethylphosphonochloridate (**10**)[3] (not purified; *ca.* 10 mmol) dissolved in benzene (5 ml) was mixed with t-butylamine (5.5 g, 80 mmol) at room temperature. Solid began to precipitate after 0.3 h and appeared complete within 2 h. After 3.5 h the solid was filtered off and identified as the *salt* (**11**), m.p. *ca.* 170 °C; $\nu_{max.}$(Nujol) 3 200—2 500 cm^{-1} (several maxima) (NH); $\delta_P(CHCl_3$–MeOH, 2:1) 32.9; $\delta_H(CDCl_3$–MeOH, 2:1) 1.78 (6 H, d, J_{PH} 17 Hz) and 1.35 (9 H, s) (Found: C, 33.45; H, 7.1; N, 5.7. $C_7H_{18}Cl_2NO_2P$ requires C, 33.6; H, 7.25; N, 5.6%). The ^{31}P n.m.r. spectrum of the filtrate showed a single peak (δ_P 28.4 in Bu^tNH_2–PhH); concentration and addition of ether gave more of the salt (**11**) (total 1.26 g, 50%).

Methyl N-*t-Butyl*-P-(1-*chloro*-1-*methylethyl*)*phosphonamidate* (**14**).—The salt (**11**) (1.67 g) was converted into the salt (**12**) by heating with t-butylamine (18 ml) at 65 °C for 38 h (sealed vessel).* The mixture was cooled and filtered (to remove Bu^tNH_3Cl). The filtrate was concentrated, diluted with ether, filtered again, and evaporated. The residue [containing the salt (**12**)] was dissolved in chloroform and the solution was washed with dilute HCl, dried, and concentrated; addition of ether gave *N*-t-butyl-*P*-(1-chloro-1-methylethyl)phosphonamidic acid (**13**) (0.10 g), m.p. 158—160 °C; $\nu_{max.}$(Nujol) 3 255 (NH) and 2 800—1 500 cm^{-1} (OH); $\delta_H(CDCl_3)$ 1.69 (6 H, d, J_{PH} 14 Hz) and 1.31 (9 H, s) (NH and OH not located); $\delta_P(CDCl_3)$ 31.3.

The acid (**13**), in dichloromethane, was treated with an excess of diazomethane to give the *methyl phosphonamidate* (**14**), crystallised from light petroleum (b.p. 40—60 °C), m.p. 92.5—93.5 °C (sealed tube); *m/z* 212, 214 (M^+ − Me, 100%) (M^+ not observed); $\nu_{max.}$(Nujol) 3 200 cm^{-1} (NH); $\delta_P(CDCl_3)$ 27.8; $\delta_H(CDCl_3)$ 3.68 (3 H, d, J_{PH} 14 Hz), 2.75 (br, NH), 1.71 (3 H, d, J_{PH} 15 Hz), 1.68 (3 H, d, J_{PH} 14 Hz), and 1.34 (9 H, s) (Found: C, 42.5; H, 8.4; N, 6.2. $C_8H_{19}ClNO_2P$ requires C, 42.2; H, 8.4; N, 6.15%).

Reactions of α-Chlorophosphonamidates.—(*a*) A solution of the methyl α-chlorophosphonamidate (1.0 mmol) in THF (6.7 ml) containing methanolic benzyltrimethylammonium methoxide (40% solution; 2.0 mmol, 1.0 ml) was maintained at a constant temperature and the progress of the reaction was monitored by ^{31}P n.m.r. spectroscopy. Except where otherwise indicated, only one or two products (δ_P 26—33 and/or 12—13 p.p.m.) were observed in significant yield, although in the later stages of reaction one of the products (δ_P 26—33) suffered some degradation (demethylation, giving δ_P 20—25). When ⩾95% of the substrate had been consumed the reaction mixture was either neutralised with NH_4Cl or (to reverse any demethylation) acidified with CF_3CO_2H and treated with diazomethane. Volatile material was evaporated and the solid residue was extracted several times with ether. The combined extracts were evaporated and the resulting crude product mixture was analysed by g.l.c. (3% silicone OV 225) and ^1H and ^{31}P n.m.r. spectroscopy. The separate products were isolated by partition of the mixture between dichloromethane and 0.4M aqueous HCl. The neutral product (δ_P 12—13) was obtained directly from the dichloromethane portion.

The aqueous portion was cooled in ice and made basic with ammonia; extraction with dichloromethane then afforded the basic product (δ_P 26—33). The separated products were characterised and, except for (**26**; R′ = Me) and (**26**; R′ = Bu^t), their identities were confirmed by comparison with authentic samples. The values of δ_P cited below relate to the THF–MeOH reaction mixtures; they are generally 0.5—1.0 p.p.m. smaller (higher field) than for the pure isolated compounds in $CDCl_3$ or CH_2Cl_2.

Methyl N-*t-butyl*-P-(*chloromethyl*)*phosphonamidate* (**7**; R = H) (δ_P 22.7; R_t 7.2 min at 135 °C) was consumed during 1.5 h at 50 °C and gave, after treatment of the reaction mixture with diazomethane, a 62:38 mixture of *dimethyl* N-*t-butyl*-N-*methylphosphoramidate* (**21**; R = H) (δ_P 12.3; R_t 2.2 min) (46% isolated), b.p. 105 °C (oven temp.) at 10 mmHg; *m/z* 195 (M^+, 1%) and 180 (M^+ − Me, 100); $\delta_H(CDCl_3)$ 3.59 (6 H, d, J_{PH} 11 Hz), 2.67 (3 H, d, J_{PH} 9 Hz), and 1.27 (9 H, s) (Found: C, 40.1; H, 9.1; N, 6.6%; M^+, 195.1022. $C_7H_{18}NO_3P$·0.8H_2O requires C, 40.1; H, 9.35; N, 6.7%; $C_7H_{18}NO_3P$ requires *M*, 195.1024) and *dimethyl* (*t-butylamino*)*methylphosphonate* (**20**; R = H) (δ_P 29.3;

* No attempt was made to optimise the yield of the salt (**12**); we now have reason to believe that a lower temperature and/or a shorter reaction time would prove much more satisfactory.

R_t 4.8 min) (28% isolated); *m/z* 195 (M^+, 2%), 180 (30), 86 ($Bu^tNHCH_2^+$, 45), and 70 (100); $\nu_{max.}$ 3 300 cm^{-1} (NH); $\delta_H(CDCl_3)$ 3.74 (6 H, d, J_{PH} 11 Hz), 2.90 (2 H, d, J_{PH} 15 Hz), 1.2 (br, NH), and 1.06 (9 H, s); *picrate*, m.p. 182—183 °C (Found: C, 36.8; H, 4.9; N, 13.3. $C_{13}H_{21}N_4O_{10}P$ requires C, 36.8; H, 5.0; N, 13.2%).

Methyl N-*t*-*butyl*-P-(1-*chloroethyl*)*phosphonamidate* (**7**; R = Me) (mixture of diastereoisomers; δ_P 25.0 and 25.4; R_t 6.5 and 7.2 min at 135 °C) was consumed during 1.3 h at 50 °C and gave, after treatment of the reaction mixture with diazomethane, a 10:90 ratio of *dimethyl* N-*t*-*butyl*-N-*ethylphosphoramidate* (**21**; R = Me) (δ_P 12.4; R_t 3.3 min) (10% isolated, but contaminated with some unchanged reactant), b.p. 110 °C (oven temp.) at 10 mmHg; *m/z* 209 (M^+, 2%) and 194 (M^+ − Me, 100); $\delta_H(CDCl_3)$ 3.64 (6 H, d, J_{PH} 11 Hz), 3.11 (2 H, dq, J_{PH} 14, J_{HH} 7 Hz), 1.27 (9 H, s), and 1.14 (3 H, t, J_{HH} 7 Hz) (Found: C, 44.7; H, 9.5; N, 6.5%; M^+, 209.1204. $C_8H_{20}NO_3P{\cdot}0.3H_2O$ requires C, 44.8; H, 9.7; N, 6.5%; $C_8H_{20}NO_3P$ requires *M*, 209.1181) and *dimethyl* 1-(*t*-*butylamino*)*ethylphosphonate* (**20**; R = Me) (δ_P 30.3; R_t 4.8 min) (66% isolated), m.p. *ca.* 32 °C; *m/z* 209 (M^+, <1%), 100 ($Bu^tNHCHMe^+$, 18), and 84 (100); $\nu_{max.}$(melt) 3 310 cm^{-1} (NH); $\delta_H(CDCl_3)$ 3.80 (3 H, d, J_{PH} 10 Hz), 3.70 (3 H, d, J_{PH} 10 Hz), 3.05 (1 H, dq, J_{PH} 18, J_{HH} 7 Hz), 1.31 (3 H, dd, J_{PH} 18, J_{HH} 7 Hz), ~1.1 (br, NH), and 1.07 (9 H, s); *picrate*, m.p. 131—132 °C (Found: C, 38.4; H, 5.2; N, 12.8. $C_{14}H_{23}N_4O_{10}P$ requires C, 38.4; H, 5.3; N, 12.8%).

Methyl N-*t*-*butyl*-P-(1-*chloro*-1-*methylethyl*)*phosphonamidate* (**14**) (δ_P 27.9) was consumed during 1.2 h at 50 °C and gave *dimethyl* 1-(*t*-*butylamino*)-1-*methylethylphosphonate* (**26**; R′ = Bu^t) (δ_P 30.8) (49% isolated; *ca.* 70% by ^{31}P n.m.r.) as an oil, *m/z* 98 (100%) (M^+ not observed); $\delta_H(CDCl_3)$ 3.77 (6 H, d, J_{PH} 10 Hz), 1.44 (6 H, d, J_{PH} 17 Hz), 1.3 (NH), and 1.17 (9 H, s); *picrate*, m.p. 123—124 °C (Found: C, 39.8; H, 5.6; N, 12.3. $C_{15}H_{25}N_4O_{10}P$ requires C, 39.8; H, 5.6; N, 12.4%); the ^{31}P n.m.r. spectrum of the reaction mixture indicated several minor products (δ_P 22.0, 10.0, and 4.3) as well as some demethylation (δ_P 24.9) of the major product.

Methyl N-*methyl*-P-(1-*chloro*-1-*methylethyl*)*phosphonamidate* (**16**) (δ_P 30.0) was converted during 0.5 h at 50 °C into *dimethyl* 1-(*methylamino*)-1-*methylethylphosphonate* (**26**; R′ = Me) (δ_P 33.0; R_t 16.5 min at 80 °C) (60% isolated; incomplete recovery from aqueous solution by dichloromethane extraction), b.p. 80 °C (oven temp.) at 0.1 mmHg; *m/z* 181 (M^+, 2%), 72 ($MeNHCMe_2^+$, 100), and 56 (80); $\nu_{max.}$ 3 320 cm^{-1} (NH); $\delta_H(CDCl_3)$ 3.72 (6 H, d, J_{PH} 10 Hz), 2.39 (3 H, s), 1.53 (1 H, s, NH), and 1.27 (6 H, d, J_{PH} 17 Hz); *picrate*, m.p. 147—148 °C (Found: C, 35.5; H, 4.7; N, 13.55. $C_{12}H_{19}N_4O_{10}P$ requires C, 35.1; H, 4.7; N, 13.7%). A minor product (δ_P 4.0) (*ca.* 10%) was also formed but was not extracted into ether in the work-up. It was not identified, although it was shown not to be dimethyl *N*-isopropyl-*N*-methylphosphoramidate (**27**; R′ = Me) (δ_P 12.4 for an authentic sample) or a degradation product thereof.

Methyl N-*t*-*butyl*-P-(1-*chloro*-1-*phenylmethyl*)*phosphonamidate* (**7**; R = Ph) (mixture of diastereoisomers; δ_P 21.5 and 21.8) was converted during 0.5 h at 25 °C into *dimethyl* N-*benzyl*-N-*t*-*butylphosphoramidate* (**21**; R = Ph) (δ_P 13.2; R_t 17.4 min at 150 °C) (96% isolated), b.p. 110 °C (oven temp.) at 0.1 mmHg; *m/z* 271 (M^+, 2%), 256 (M^+ − Me, 30), and 91 ($PhCH_2^+$, 100); $\delta_H(CDCl_3)$ 7.4—7.1 (5 H, m), 4.33 (2 H, d, J_{PH} 12 Hz), 3.62 (6 H, d, J_{PH} 11 Hz), and 1.25 (9 H, s) (Found: C, 57.05; H, 8.2; N, 5.1. $C_{13}H_{22}NO_3P$ requires C, 57.55; H, 8.2; N, 5.2%). Both ^{31}P n.m.r. spectroscopy and g.l.c. suggested a trace amount (*ca.* 1%) of dimethyl 1-(t-butylamino)-1-phenylmethylphosphonate (**20**; R = Ph) (δ_P 26.0; R_t 14.6 min; same values for authentic sample) but it was not isolated. When the reaction was carried out in methanol containing sodium methoxide (1.8M solution; 5 mol equiv.) at 50 °C for 1.25 h, an 88:12 mixture of (**21**; R = Ph) and (**20**; R = Ph) was obtained. Partition of the product between dichloromethane and aqueous HCl afforded the phosphoramidate (**21**; R = Ph) (82% isolated) and the *phosphonate* (**20**; R = Ph) (9% isolated), m.p. 90.5—91.5 °C (from light petroleum); *m/z* 161 [M^+ − $HP(O)(OMe)_2$, 10%] and 146 (100) (M^+ not observed); $\nu_{max.}$(Nujol) 3 315 cm^{-1} (NH); $\delta_H(CDCl_3)$ 7.5—7.1 (5 H, m), 4.13 (1 H, d, J_{PH} 26 Hz), 3.74 (3 H, d, J_{PH} 10 Hz), 3.43 (3 H, d, J_{PH} 10 Hz), 1.75 (NH), and 0.96 (9 H, s) (Found: C, 57.8; H, 8.15; N, 5.1. $C_{13}H_{22}NO_3P$ requires C, 57.55; H, 8.2; N, 5.2%).

(b) *Ethyl* N-*t*-*butyl*-P-(1-*chloroethyl*)*phosphonamidate* (mixture of diastereoisomers; δ_P 24.9 and 25.0; R_t 6.8 and 7.4 min at 135 °C) was heated in ethanol containing sodium ethoxide (1.2M solution; 4 mol equiv) During 0.8 h at 75 °C it was converted into a 17:83 mixture (^{31}P n.m.r.) of *diethyl* N-*t*-*butyl*-N-*ethylphosphoramidate* (**25**) (δ_P 9.4; R_t 3.6 min) (13% isolated), b.p. 110 °C (oven temp.) at 9 mmHg; *m/z* 237 (M^+, 8%) and 222 (M^+ − Me, 100); $\delta_H(CDCl_3)$ 4.00 (4 H, dq, $J_{PH} \sim J_{HH} \sim 7$ Hz), 3.12 (2 H, dq, J_{PH} 14, J_{HH} 7 Hz), 1.30 (6 H, t, J_{HH} 7 Hz), 1.28 (9 H, s), and 1.15 (3 H, t, J_{HH} 7 Hz) (Found: C, 49.5; H, 10.1; N, 5.8%; M^+, 237.1494. $C_{10}H_{24}NO_3P{\cdot}0.3H_2O$ requires C, 49.5; H, 10.2; N, 5.8%; $C_{10}H_{24}NO_3P$ requires *M*, 237.1494) and *diethyl* 1-(*t*-*butylamino*)*ethylphosphonate* (**24**) (δ_P 28.1; R_t 5.8 min) (58% isolated), *m/z* 237 (M^+, 3%), 100 ($Bu^tNHCHMe^+$, 100), and 84 (80); $\nu_{max.}$ 3 300 cm^{-1} (NH); $\delta_H(CDCl_3)$ 4.16 (2 H, dq, $J_{PH} \sim J_{HH} \sim 7$ Hz), 4.08 (2 H, dq, $J_{PH} \sim J_{HH} \sim 7$ Hz), 3.02 (1 H, dq, J_{PH} 19, J_{HH} 7 Hz), 1.75 (br, NH), 1.32 (3 H, dd, J_{PH} 18, J_{HH} 7 Hz), 1.30 (6 H, t, J_{HH} 7 Hz), and 1.07 (9 H, s); *picrate*, m.p. 115—117 °C (Found: C, 41.3; H, 5.8; N, 12.2. $C_{16}H_{27}N_4O_{10}P$ requires C, 41.2; H, 5.8; N, 12.0%). Some degradation (5—10%) of the major product (δ_P 28.1 converted into δ_P 24.3) was apparent in the later stages of the reaction.

Authentic Samples of α-(t-Butylamino)phosphonates.—The imines were prepared from t-butylamine and formaldehyde,[18,19] acetaldehyde,[19,20] or benzaldehyde.[21] While stirring and cooling, dimethyl or diethyl phosphite was mixed with the appropriate imine (1 mol equiv. or a small excess), and the mixture was left at room temperature overnight. The products (**20**; R = H), (**20**; R = Me), and (**24**) were isolated by vacuum distillation, (**20**; R = Ph) by crystallisation. Their characteristics were the same as those of the α-(t-butylamino)-phosphonates isolated from the rearrangements of the α-chlorophosphonamidates.

Authentic Samples of Phosphoramidates.—Dimethyl *N*-t-butylphosphoramidate, m.p. 72—73 °C (lit.,[22] m.p. 64—65 °C), diethyl *N*-t-butylphosphoramidate, b.p. 80 °C (oven temp.) at 0.5 mmHg (lit.,[23] b.p. 95 °C at 1 mmHg), and dimethyl *N*-isopropylphosphoramidate, b.p. 130 °C (oven temp.) at 3.5 mmHg, m.p. *ca.* 36 °C (lit.,[24] b.p. 107—109 °C at 1 mmHg, m.p. 42 °C) were prepared from dimethyl or diethyl phosphorochloridate and the appropriate amine. These *N*-alkylphosphoramidates were converted into *N,N*-dialkylphosphoramidates by the following procedure. The *N*-alkylphosphoramidate (2.5 mmol) was added in portions to a stirred suspension of sodium hydride (5 mmol) in dimethylformamide (3 ml). After 15 min the alkyl halide [methyl or ethyl iodide (an excess) or benzyl bromide (2.5 mmol)] was cautiously introduced and the mixture was stirred for 2—3 h. Benzene (15 ml) and water (15 ml) containing ammonium chloride (2.5 mmol) were carefully added, and the organic layer was separated and washed with water (2 or 3 × 2 ml portions) to remove the remaining dimethylformamide (some of the product was also removed). The solution was dried (Na_2SO_4) and the hygroscopic *N,N*-dialkylphosphoramidate was isolated by distillation under reduced pressure. For (**21**; R = H), (**21**; R =

Me), (**21**; R = Ph), and (**25**) the material obtained in this way was the same as that isolated from the appropriate α-chlorophosphonamidate rearrangement. *Dimethyl* N-*isopropyl*-N-*methylphosphoramidate* (**27**; R′ = Me) was not a rearrangement product; it had b.p. 105 °C (oven temp.) at 10 mmHg; *m*/*z* 181 (M^+, 7%) and 166 (M^+ − Me, 100); $\delta_H(CDCl_3)$ *ca.* 3.8 (1 H, m), 3.60 (6 H, d, J_{PH} 11 Hz), 2.48 (3 H, d, J_{PH} 10 Hz), and 1.09 (6 H, d, J_{HH} 7 Hz) (Found: C, 38.9; H, 9.0; N, 7.5; M^+, 181.0873. $C_6H_{16}NO_3P{\cdot}0.25H_2O$ requires C, 38.8; H, 9.0; N, 7.5%; $C_6H_{16}NO_3P$ requires *M*, 181.0868).

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