Migration of a Benzyl Group in the Lossen-like Rearrangement of an *N*-Phosphinoyl-*O*-sulphonylhydoxylamine

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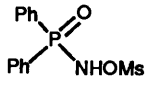
Migration of a group other than aryl has been observed for the first time in the Lossen-like rearrangement of an *N*-phosphinoyl-*O*-sulphonylhydroxylamine: the benzylic substrate $(ArCH_2)_2P(O)NHOMs$ (Ar = *p*-tolyl) gives the phosphonamidate $ArCH_2P(O)(OR)NHCH_2Ar$ (**14**) on treatment with alkoxide. The benzyl group seems to migrate less readily than aryl, so rearrangement is relatively slow and competing reactions can be of major importance. Thus, while with isopropoxide or t-butoxide the phosphonamidate (**14**; R = Pr^i or Bu^t) is formed in 70–80% yield, with methoxide or ethoxide the rearrangement accounts for only 25–35% and major amounts of $(ArCH_2)_2P(O)OR$ (R = Me or Et) and $(ArCH_2)_2P(O)NH_2$ are formed. Rearrangement is even less important with t-butylamine, the hydrazide $(ArCH_2)_2P(O)NHNHBu^t$ being much the most abundant product. The fact that a benzyl group can migrate is mechanistically significant; it shows that the migration centre can be a saturated (sp^3) carbon atom, and that the new bond to nitrogen can be formed without direct involvement of π electrons.

When suitably activated, *N*-phosphinoylhydroxylamines such as $Ph_2P(O)NHOH$ undergo Lossen-like rearrangement. Thus, for example, a phenyl group migrates from phosphorus to nitrogen when the *O*-methanesulphonate (**1**) is treated with sodium methoxide or t-butylamine.[1] The monomeric metaphosphonimidate (**2**) is presumably formed initially, but the observed product is the phosphonamidate (**3**; X = MeO) or phosphonic diamide (**3**; X = Bu^tNH).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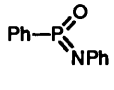
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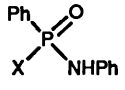
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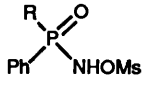
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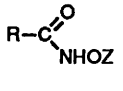
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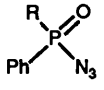
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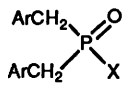
An unsymmetrical substrate (**4**), in which R is a simple alkyl group (Me,Et,Pr^i), can, in principle, rearrange in two ways. In practice, however, only the product of Ph migration is formed; no migration of the alkyl group has ever been observed.[2] This highly selective migration is notable on two counts: (i) hydroxamic acid derivatives (**5**; Z = COPh *etc.*) undergo the Lossen rearrangement as readily when the migrating group (R) is alkyl as when it is phenyl;[3] (ii) the unsymmetrical phosphinic azides (**6**) undergo photochemical Curtius rearrangements in which migration of the alkyl group R is not only as important as Ph migration, but is actually somewhat preferred.[4]

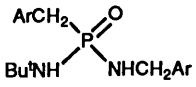
To further our understanding of the mechanism of the Lossen-like rearrangement, we need to know whether there is an insurmountable barrier to alkyl migration. We must therefore look at dialkylphosphinoylhydroxylamine derivatives, to see if alkyl migration will occur when no alternative rearrangement pathway is available.

Results and Discussion

Repeated attempts to prepare simple *N*-dialkylphosphinoylhydroxylamines [$R_2P(O)NHOH$; R = Et or Pr^i] from the phosphinic chlorides [$R_2P(O)Cl$] and $H_2NOSiMe_3$ proved unsuccessful, apparently because of steric inhibition of nucleophilic attack at phosphorus (R = Pr^i) or decomposition during removal of the trimethylsilyl blocking group (R = Et). The benzylic compound (**8**), however, could be obtained in good yield (73%) from the phosphinic chloride (**7**), and on treatment with $MeSO_2Cl$ in pyridine it gave the methanesulphonate (**9**).†


(7) X = Cl
(8) X = NHOH
(9) X = NHOMs

(10) X = $NHNHBu^t$
(11) X = NHOMe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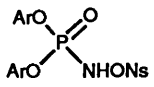
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Ar = *p*-tolyl

When dissolved in a large excess of t-butylamine the methanesulphonate (**9**) (δ_p 44.8) was consumed during *ca.* 30 min at room temperature. A single product (δ_p 41.7, 80%) was seen to dominate the reaction mixture; it was isolated and characterised as the phosphinoylhydrazine (**10**). For confirmation of its structure, the product was compared with a sample of (**10**) prepared in a more conventional way, *viz.* reaction of the phosphinic chloride (**7**) with t-butylhydrazine.

Four minor products were also detected (^{31}P NMR) in the reaction of the methanesulphonate, and two of these had chemical shifts (δ_p 27.3 and 23.4) of the order expected for the phosphonic diamide rearrangement product (**12**). However,

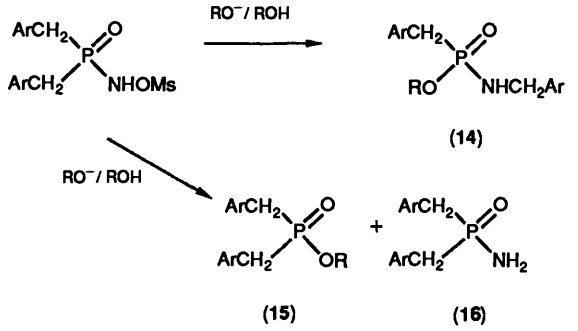
† We chose to work with the 4-methylbenzyl group rather than simple benzyl because in preliminary experiments the phosphinoylhydroxylamine (**8**) was obtained in better yield with $ArCH_2$ = 4-methylbenzyl. Also, it seemed possible that methyl groups would prove advantageous in ^1H NMR studies. We would not expect the chemistry to be influenced to any significant extent by the presence of 4-methyl substituents.

since the yield of each of the minor products was only *ca.* 5%, it is clear that rearrangement is of minor importance, if it occurs at all. Use of just 2 equiv. of t-butylamine in dichloromethane solution did not increase the amount of rearrangement; on the contrary, the phosphinoylhydrazine became even more dominant (>90%) and only one minor product [the phosphinic amide (**16**)] was formed in any significant amount.

Displacement of the sulphonyl leaving group, by nucleophilic attack at nitrogen, is the simplest explanation for formation of the phosphinoylhydrazine. In principle, the methanesulphonates (**1**) and (**4**) can also react in this way with amines; the fact that they do not is doubtless a consequence of easy phenyl migration making their rearrangements very fast.[1,2] Compared with (**9**), the reactions of (**1**) and (**4**) certainly seem to be very rapid; with neat t-butylamine they react more or less as quickly as they dissolve.[1,2]

We have previously encountered hydrazide formation only with phosphoryl substrates such as (**13**), which show no tendency to rearrange (ArO migration).[5] For them the absence of rearrangement is hardly surprising, given that *N*-acylhydroxylamine derivatives do not undergo Lossen rearrangement if it would require migration of a phenoxy (or alkoxy) group.[6] For benzyl groups, however, migration occurs without apparent difficulty in the Lossen rearrangement.[3]

Treatment with sodium methoxide (2 mol equiv.) in methanol (15 min at room temperature) transformed the methanesulphonate (**9**) into a mixture of products (^{31}P NMR) having three principal components (≥20%) and two minor ones (~10%). Samples of the principal products were isolated by TLC and crystallisation. Two were identified simply as the phosphinic ester (**15**; R = Me) and the phosphinic amide (**16**) (Scheme 1) but the third was more interesting: it had an amide N–H (ν_{max} 3 180 cm^{-1}), a *P*-methoxy group (δ 3.56, d, J_{PH} 10



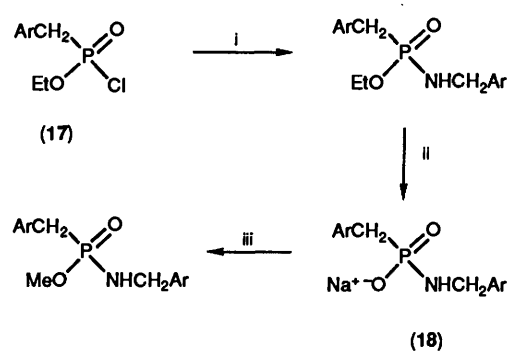
Scheme 1.

Hz), and two dissimilar $ArCH_2$ groups, one still attached directly to the P atom (δ 3.05, d, J_{PH} 20 Hz), the other separated from it by the NH group (δ 3.95, dd, $J_{PH} \sim J_{HH} \sim 7$ Hz). Also, in the mass spectrum the most abundant fragment (*m/z* 120) had a mass corresponding to the ion $ArCH_2NH^+$. These features clearly point to the phosphonamidate structure (**14**; R = Me), the product that would result from a Lossen-like rearrangement. The structure of the product was confirmed by comparison with an authentic sample of (**14**; R = Me), prepared from the available phosphonochloridate (**17**) (Scheme 2). The approximate contribution of each of the principal products to the total reaction mixture, deduced from the ^{31}P NMR spectrum with support from GLC, is shown in the Table.

* With a powerful hydride donor ($NaBH_4$ in MeOH) the methanesulphonate is converted rapidly and cleanly into the amide (**16**).

Table. Alkoxide-induced reactions of $(ArCH_2)_2P(O)NHOMs$ (**9**) in ROH; approx. yields (%) of principal products.

	R = Me	R = Et	R = Pr^i	R = Bu^t
Phosphonamidate (**14**)	25	35	70	80
Phosphinic ester (**15**)	35	15	Trace	0
Phosphinic amide (**16**)	20	30	15	0



Scheme 2. *Reagents:* i, $ArCH_2NH_2$, Et_3N; ii, NaOH; iii, CF_3CO_2H, CH_2N_2

As with t-butylamine, nucleophilic attack on the substrate seems to be the single most important process. Now, however, the attack is at phosphorus, not at nitrogen, and results in the ester (**15**; R = Me). If attack were to occur at nitrogen, the *N*-methoxyamide (**11**) would be formed. This might be unstable in the presence of methoxide, undergoing base-induced fragmentation to give the amide (**16**) and H_2CO. We therefore examined a sample of (**11**), prepared from the phosphinic chloride (**7**) and H_2NOMe. This established not only that (**11**) was completely absent from the products of the methanesulphonate reaction, but also that, if it had been formed, it would have been stable under the conditions of the reaction. Notwithstanding, nucleophilic attack at the N atom of the substrate may still be important: if the nucleophile were hydride, supplied by the alkoxide ion, the amide (**16**) would be formed directly.*

As well as P and N, the S atom of the methanesulphonate (**9**) is a possible site of nucleophilic attack. This would result in desulphonylation and release of the phosphinoylhydroxylamine (**8**). In control experiments the phosphinoylhydroxylamine (δ_p 50.3 in MeOH) was found, as expected,[7] to be unstable in NaOMe solution. It was rapidly transformed into a labile substance (δ_p 58.9) [probably $(ArCH_2)_2P(O)ONH_2$ – *cf.* ref. 7] which decomposed over 10 min to give largely the phosphinate anion $[(ArCH_2)_2P(O)O^-]$. This anion was also a product of the methanesulphonate reaction, but the amount (~5%) implies that desulphonylation was not a major pathway.

With ethoxide in ethanol, rearrangement, giving the phosphonamidate (**14**; R = Et), was the single most important reaction of the methanesulphonate (**9**), but it still only accounted for about one-third of the total product (Table). Competing nucleophilic attack at phosphorus was practically eliminated on going to isopropoxide [trace only of ester (**15**; R = Pr^i)], and rearrangement to give (**14**; R = Pr^i) became much the most important reaction (Table). Finally, with KOBu^t–Bu^{t}OH, amide formation was also suppressed, and the rearrangement product (**14**; R = Bu^t) was formed in 80% yield.

With both isopropoxide and t-butoxide, the ^{31}P NMR spectrum showed an appreciable minor product (~10%) at an even higher field ($\delta_p \sim 20$) than the phosphonamidate (**14**). This too must be a product of rearrangement. In fact, it seems it is the anion of the phosphonamidic acid, since addition of the salt (**18**)

to the reaction mixture increased the size of the signal. It could result from the monomeric metaphosphonimidate being trapped by water present in the alcohol solvents, although the amount of water must have been very small, and 3-co-ordinate P^V species usually react rather indiscriminately with nucleophiles.[8] Alternatively, it might be formed *via* a mixed phosphonamidic-sulphonic anhydride (*cf.* discussion in ref. 5).

Conclusion

The conclusion to be drawn from this study is that benzyl groups can migrate in Lossen-like rearrangements of *N*-phosphinoylhydroxylamine derivatives. In our earlier study of the unsymmetrical substrates ArPhP(O)NHOMs we found that substituents have a rather large effect on the migratory aptitude of the Ar group relative to Ph, and that the nature of the effect (correlation with σ^+, $\rho \sim -1.7$) implies a substantial involvement of the π system in the transition state for rearrangement.[9] Our present results accord with that picture: if π electrons are available, they participate and make migration easy; if they cannot participate directly, as with the benzyl group, migration will still occur, but only with some reluctance.

Experimental

Instrumentation was generally as described before.[9] IR spectra were recorded as Nujol mulls. The ^{31}P NMR spectra (^1H-decoupled) were recorded at 36.2 MHz with a JEOL JNM-FX90Q spectrometer; positive chemical shifts are downfield from external 85% H_3PO_4. t-Butylamine was dried over KOH and distilled. Methanol and ethanol were dried by distillation from their magnesium salts, isopropyl alcohol and t-butyl alcohol by storage over powdered 3A molecular sieve for several days. Potassium t-butoxide was purified by sublimation. The reactions of the methanesulphonate (**9**) were carried out in as near anhydrous conditions as possible. The phosphonochloridate (**17**) was available from other work.[10]

Bis(4-methylbenzyl)phosphinic Acid.—Dibutyl phosphite (12.6 g, 65 mmol) in benzene (60 ml) was added dropwise with stirring (powerful magnetic stirrer) to a solution of the Grignard reagent prepared from 4-methylbenzyl chloride (28.1 g, 200 mmol) and magnesium (4.8 g) in ether (120 ml). The ether refluxed gently and much solid precipitated. When addition was complete (25 min) the mixture was refluxed for a further 1 h. It was then cooled in ice and stirred while aqueous sulphuric acid (19 ml conc. H_2SO_4 in 57 ml water) was dripped in over 20 min. The two layers were separated and the aqueous portion was extracted with dichloromethane. The original organic portion and the dichloromethane extract were washed with water, combined, dried (Na_2SO_4), and concentrated to an oil. Addition of light petroleum precipitated bis(4-methylbenzyl)-phosphine oxide (12.0 g, 72%), m.p. 99–100 °C; $\delta_p(CH_2Cl_2)$ 35.6; $\delta(CDCl_3)$ 7.32 (1 H, d × quintet, J_{PH} 464, J_{HH} 3 Hz), 7.01 (8 H, s), 3.11 (4 H, dd, J_{PH} 15, J_{HH} 3 Hz), and 2.29 (6 H, d, J_{PH} 2 Hz).

A solution of the phosphine oxide (8.3 g, 32.2 mmol) in methanol (12 ml) was heated (bath temp. ~ 90 °C) and stirred while hydrogen peroxide (30% w/v; 4.8 ml, 42 mmol) was added dropwise over 0.5 h. Heating was continued for a further 1.5 h. The mixture was then cooled and the solid filtered off, washed with aqueous methanol, and crystallised from toluene to give bis(4-methylbenzyl)phosphinic acid (6.6 g, 75%), m.p. 175–176 °C (lit.,[11] 173–174 °C); $\delta_p(CH_2Cl_2)$ 51.0; $\delta(CDCl_3)$ 10.28 (1 H, s), 7.02 (8 H, s), 2.80 (4 H, d, J_{PH} 17 Hz), and 2.26 (6 H, d, J_{PH} 2 Hz).

Bis(4-methylbenzyl)phosphinic Chloride (**7**).—Oxalyl chloride (1.27 g, 10 mmol) was added in small portions to a stirred solution of the phosphinic acid (1.92 g, 7.0 mmol) in dichloromethane (20 ml). Reaction was quite vigorous and gas was evolved. After a further 1 h the volatile material was evaporated. Residual traces of oxalyl chloride were removed by addition and evaporation of carbon tetrachloride, followed by pumping *in vacuo* (0.2 mmHg, 2 h). The phosphinic chloride (**7**) was obtained as a spectroscopically pure solid, m.p. *ca.* 125 °C; *m/z* 294, 292 (M^+, 10%), and 105 (100); ν_{max} 1 235 cm^{-1} (P=O); $\delta_p(CH_2Cl_2)$ 61.5; $\delta(CDCl_3)$ 7.07 (8 H, s), 3.34 (4 H, d, J_{PH} 14 Hz), and 2.27 (6 H, d, J_{PH} 3 Hz).

N-[*Bis(4-methylbenzyl)phosphinoyl*]*hydroxylamine* (**8**).—A mixture of *O*-trimethylsilylhydroxylamine (0.89 g, 8.5 mmol) and triethylamine (0.76 g, 7.5 mmol) in dichloromethane (16 ml) was stirred at 0 °C while bis(4-methylbenzyl)phosphinic chloride (**7**) (7.0 mmol) in dichloromethane (8 ml) was added dropwise over 15 min. The mixture was allowed to warm to room temperature, and stirring was continued for a further 1 h. Desilylation was accomplished by adding methanol (4 ml). After 8 min volatile material was evaporated (no heat) and (to ensure complete desilylation) more methanol (*ca.* 5 ml) was added and evaporated. The sticky residue was washed as thoroughly as possible with iced water. On trituration with methanol a solid was then obtained. The methanol was carefully diluted with a little water and the solid collected, giving the *phosphinoylhydroxylamine* (**8**) (1.46 g, 73%), m.p. 118–119 °C (decomp.); *m/z* (FAB; glycerol matrix) 290 ($M + H^+$, 100%), 274 (30), 120 (10), and 105 (80); ν_{max} 3 185 cm^{-1}; $\delta_p(CH_2Cl_2)$ 49.4; $\delta(CDCl_3)$ 8.06 br (1 H, s), 7.03 (8 H, s), 5.53 (1 H, d, J_{PH} 7 Hz), 3.02 (4 H, d, J_{PH} 15 Hz), and 2.22 (6 H, d, J_{PH} 2 Hz) (Found: C, 62.6; H, 7.2; N, 4.5; $C_{16}H_{20}NO_2P{\cdot}H_2O$ requires C, 62.5; H, 7.2; N, 4.6%).

N-[*Bis(4-methylbenzyl)phosphinoyl*]-O-*methylsulphonylhydroxylamine* (**9**).—While cooling in ice, the phosphinoylhydroxylamine (**8**) (289 mg, 1.0 mmol) was mixed with pyridine (0.8 ml) and methanesulphonyl chloride (160 mg, 1.4 mmol) was immediately added. Cooling and mixing were continued for *ca.* 10 min. Some of the pyridine was removed *in vacuo* (no heat) and iced water (8 ml) was then added, mixed thoroughly, and decanted off. The residual oil solidified on trituration with methanol. Crystallisation from benzene gave the *methanesulphonate* (**9**) (143 mg, 39%), m.p. 131–132 °C (decomp.); ν_{max} 2 780 cm^{-1}; $\delta_p(CH_2Cl_2)$ 48.0; $\delta(CDCl_3)$ 8.20 (1 H, d, J_{PH} 5 Hz), 7.17 (8 H, s), 3.23 (4 H, d, J_{PH} 15 Hz), 3.10 (3 H, s), and 2.37 (6 H, d, J_{PH} 2 Hz) (Found: C, 55.7; H, 6.0; N, 3.8. $C_{17}H_{22}NO_4PS$ requires C, 55.6; H, 6.0; N, 3.8%).

Authentic Samples of Potential Products of Reactions of the Methanesulphonate (**9**).—The compounds below were prepared by treatment of bis(4-methylbenzyl)phosphinic chloride (**7**) with NH_3, RONa–ROH (R = Me, Et, or Pr^i), or KOBu^t–Bu^{t}OH following conventional procedures. The ^1H NMR spectra of (**15**) contained the expected 4-methylbenzyl signals [δ 7.05 (8 H, s), 2.95 (4 H, d, J_{PH} 16 Hz), and 2.30 (6 H, d, J_{PH} 2 Hz)] in addition to those shown, and the i.r. spectra included ν_{max} 1 210 or 1 155 cm^{-1} [P=O in (**15**) or (**16**)].

Bis(4-methylbenzyl)phosphinic amide (**16**), m.p. 142–144 °C (from benzene); *m/z* 273 (M^+, 20%) and 105 (100); ν_{max} 3 360, 3 280, 3 190, and 3 080 cm^{-1} (all br; NH); $\delta_p(CDCl_3)$ 36.3; $\delta(CDCl_3)$ 7.05 (8 H, s), 2.97 (4 H, d, J_{PH} 15 Hz), 2.70 (2 H, br s), and 2.30 (6 H, d, J_{PH} 2 Hz) (Found: C, 70.6; H, 7.8; N, 5.2. $C_{16}H_{20}NOP$ requires C, 70.3; H, 7.4; N, 5.1%).

Methyl bis(4-methylbenzyl)phosphinate (**15**; R = Me), m.p. 109–110 °C (from light petroleum); *m/z* 288 (M^+, 40%) and 105 (100); $\delta_p(CDCl_3)$ 49.6; $\delta(CDCl_3)$ 3.52 (3 H, d, J_{PH} 10 Hz, OMe) (Found: C, 70.65; H, 7.5. $C_{17}H_{21}O_2P$ requires C, 70.8; H, 7.3%).

Ethyl bis(4-methylbenzyl)phosphinate (**15**; R = Et), m.p. 72–73 °C (from light petroleum); *m/z* 302 (M^+, 30%), 274 (10), and 105 (100); $\delta_p(CDCl_3)$ 48.4; $\delta(CDCl_3)$ 3.85 (2 H, dq, J_{PH} = J_{HH} = 7 Hz) and 1.14 (3 H, t, J_{HH} 7 Hz) (OEt) (Found: C, 71.3; H, 7.45. $C_{18}H_{23}O_2P$ requires C, 71.5; H, 7.7%).

Isopropyl bis(4-methylbenzyl)phosphinate (**15**; R = Pr^i), m.p. 101–102 °C (from light petroleum); *m/z* 316 (M^+, 30%), 274 (30), and 105 (100); $\delta_p(CDCl_3)$ 47.4; $\delta(CDCl_3)$ 4.48 (1 H, d × sept, $J_{PH} \sim J_{HH} \sim 6$ Hz) and 1.12 (6 H, d, J_{HH} 6 Hz) (OPr^i) (Found: C, 72.1; H, 8.0. $C_{19}H_{25}O_2P$ requires C, 72.1; H, 8.0%).

t-Butyl bis(4-methylbenzyl)phosphinate (**15**; R = Bu^t), m.p. 141–142 °C (from light petroleum); *m/z* 330 (M^+, 10%), 274 (50), and 105 (100); $\delta_p(CDCl_3)$ 45.0; $\delta(CDCl_3)$ 1.28 (9 H, s, OBu^t) [not formed in the reactions of the methanesulphonate (**9**)].

Ethyl N,P-*Bis(4-methylbenzyl)phosphonamidate* (**14**; R = Et).—A solution of ethyl 4-methylbenzylphosphonochloridate (**17**) (1.86 g, 8 mmol) in CH_2Cl_2 (8 ml) was added dropwise with stirring to a cooled mixture of 4-methylbenzylamine (1.21 g, 10 mmol) and triethylamine (1.01 g, 10 mmol) in CH_2Cl_2 (15 ml). After a further 15 min, at room temperature, the mixture was diluted with ether and filtered. The filtrate was evaporated and the residue, dissolved in CH_2Cl_2, was washed with water containing just sufficient HCl to keep it acidic. Crystallisation from light petroleum then gave the *ethyl phosphonamidate* (**14**; R = Et) (2.03 g, 80%), m.p. 85.5–86.5 °C; *m/z* 317 (M^+, 20%), 120 (100), and 105 (60); ν_{max} 3 220 cm^{-1} (NH); $\delta_p(CDCl_3)$ 29.9; $\delta(CDCl_3$, 300 MHz) 7.15–7.05 (8 H, m), 4.01 (2 H, m, OCH_2Me), 3.99 (2 H, dd, $J_{PH} \sim J_{HH} \sim 7$ Hz, $NHCH_2Ar$), 3.10 (2 H, d, J_{PH} 20 Hz, PCH_2Ar), 2.65 br (m, NH), 2.32 (3 H, s), 2.31 (3 H, d, J_{PH} 2 Hz), and 1.25 (3 H, t, J_{HH} 7 Hz) (Found: C, 68.0; H, 7.6; N, 4.85. $C_{18}H_{24}NO_2P$ requires C, 68.1; H, 7.6; N, 4.4%).

Methyl N,P-*Bis(4-methylbenzyl)phosphonamidate* (**14**; R = Me).—The ethyl phosphonamidate (**14**; R = Et) (0.27 g, 0.84 mmol) was hydrolysed by heating with sodium hydroxide (0.14 g) in ethanol–water (4:1) (1.5 ml) for 4 h at 75–80 °C. The excess base was exactly neutralised with hydrochloric acid and the solution was evaporated. The residue was extracted with ethanol containing a little methanol, and the extract was concentrated to give sodium bis(4-methylbenzyl)phosphinate (**18**) (0.26 g) (possibly contaminated with a little NaCl), ν_{max} 3 420 cm^{-1} (NH); $\delta_p(CDCl_3$–$CD_3OD)$ 22.0, $\delta(CDCl_3$–$CD_3OD)$ 7.3–6.9 (8 H, m), 3.90 (2 H, d, J_{PH} 6 Hz), 2.89 (2 H, d, J_{PH} 19 Hz), and 2.24 (6 H, 2 or 3 overlapping lines).

The sodium salt (**18**) (0.17 g, 0.55 mmol) was dissolved in methanol (2 ml) at 0 °C. Trifluoroacetic acid (68 mg) was added in five portions, each portion being followed by an excess of diazomethane in ether. Volatile material was evaporated and the residue, dissolved in ether, was washed with water. Crystallisation from ether–light petroleum then gave the *methyl phosphonamidate* (**14**; R = Me) (0.098 g, 59%), m.p. 95–96 °C; *m/z* 303 (M^+, 20%), 120 (100), and 105 (35); ν_{max} 3 180 cm^{-1} (NH); $\delta_p(CDCl_3)$ 31.2; $\delta(CDCl_3)$ 7.00 (8 H, 2 or more lines), 3.95 (2 H, dd, $J_{PH} \sim J_{HH} \sim 7$ Hz, $NHCH_2Ar$), 3.56 (3 H, d, J_{PH} 10 Hz, OMe), 3.05 (2 H, d, J_{PH} 20 Hz, PCH_2Ar), 2.7 br (1 H, NH), and 2.25 (6 H, 2 or 3 overlapping lines) (Found: C, 67.6; H, 7.1; N, 4.9. $C_{17}H_{22}NO_2P$ requires C, 67.3; H, 7.3; N, 4.6%).

N-*Methoxybis(4-methylbenzyl)phosphinic Amide* (**11**).—A suspension of methoxyamine hydrochloride (84 mg, 1.0 mmol) in dichloromethane (1.5 ml) was stirred at 0 °C. Triethylamine (91 mg, 0.9 mmol) was added, followed by bis(4-methylbenzyl)-phosphinic chloride (**7**) (156 mg, 0.54 mmol). The mixture was stirred for a further 1 h at room temperature after which it was washed with water and evaporated. To remove a by-product [$\delta_p(CDCl_3)$ 48.3, believed to be the phosphinic anhydride], the crude product was dissolved in methanol and aqueous sodium hydroxide (0.1 mmol) was added. Dilution with water and crystallisation of the resulting precipitate from light petroleum–dichloromethane gave the N-*methoxyphosphinic amide* (**11**) (111 mg, 68%), m.p. 114–116 °C; *m/z* 303 (M^+, 4%), 273 ($M^+ - CH_2O$, 25), and 105 (100); ν_{max} 3 160 cm^{-1} (NH), $\delta_p(CDCl_3)$ 46.8, $\delta(CDCl_3)$ 7.03 (8 H, s), 3.61 (3 H, s), 3.06 (4 H, d, J_{PH} 15 Hz), and 2.27 (6 H, d, J_{PH} 2 Hz) (Found: C, 67.1; H, 7.25; N, 4.8. $C_{17}H_{22}NO_2P$ requires C, 67.3; H, 7.3; N, 4.6%).

Reactions of N-[*Bis(4-methylbenzyl)phosphinoyl*]-O-*methylsulphonylhydroxylamine* (**9**).—(a) *With t-butylamine.* The methanesulphonate (**9**) (78 mg, 0.21 mmol) was dissolved in t-butylamine (1.0 ml). Over a period of 0.5 h the substrate (δ_p 44.8) was converted into one principal product (δ_p 41.7; 80%) and four minor ones (δ_p 37.0, 27.3, 23.4, 16.4). Volatile material was evaporated and the residue was extracted thoroughly with light petroleum. After being washed with water the petroleum extract, which contained only one phosphorus compound, afforded N-[*bis(4-methylbenzyl)phosphinoyl*]-N′-*t-butylhydrazine* (**10**), which crystallised from aqueous methanol, m.p. 88–90 °C; *m/z* 344 (M^+, 25%), 329 (M^+ – Me, 35), 288 ($M^+ - C_4H_8$, 10), and 105 (100); ν_{max} 3 640, 3 260, and 3 230 cm^{-1} (NH); $\delta_p(CDCl_3)$ 42.4; $\delta(CDCl_3)$ 7.05 (8 H, s), 3.87 (1 H, d, J_{PH} 12 Hz, NH), 3.08 (4 H, d, J_{PH} 15 Hz), 2.7 (1 H, br, NH), 2.28 (6 H, s), and 1.02 (9 H, s) (Found: M^+, 344.2019. $C_{20}H_{29}N_2OP$ requires *M*, 344.2017).

An authentic sample of (**10**), prepared from the phosphinic chloride (**7**) and t-butylhydrazine (liberated from Bu^tNHNH_2·HCl using Et_3N in CH_2Cl_2), showed the same characteristics.

(b) *With alkoxides.* A solution of the alkoxide (~0.4M), prepared by adding NaOMe, NaH, or $KOBu^t$ (2 mol equiv.) to the appropriate alcohol, was mixed with the methanesulphonate (**9**) (1 mol equiv.). ^{31}P NMR spectroscopy was used to follow the progress of the reaction (complete in 5–20 min) and to analyse the product mixture. The excess of alkoxide was neutralised (AcOH), the solvent evaporated, and the residue partitioned between dichloromethane and water. The organic layer was separated, dried (Na_2SO_4), and concentrated. The resulting crude product was examined by GLC 3% OV 17 at 256 °C), and the phosphonamidate rearrangement products were isolated as described below. The identities of the phosphinic esters (**15**; R = Me, Et, Pr^i) (R_t 5.0–5.3 min), the phosphinic amide (**16**) (R_t 12.2 min), and the phosphonamidates (**14**; R = Me, Et) were established by comparison with the authentic samples.

With t-butoxide. The crude product consisted of a single phosphorus compound. Crystallisation from light petroleum–tetrachloromethane afforded *t-butyl* N,P-*bis(4-methylbenzyl)-phosphonamidate* (**14**; R = Bu^t), m.p. 103–104 °C; *m/z* 345 (M^+, 2%), 289 ($M^+ - C_4H_8$, 70), 288 ($M^+ - C_4H_9$, 60), 184 (50), 120 ($ArCH_2NH^+$, 100), and 105 ($ArCH_2^+$, 85); ν_{max} 3 255 cm^{-1} (NH); $\delta_p(CDCl_3)$ 25.5; $\delta(CDCl_3)$ 7.06 and 7.02 (total 8 H; 2 overlapping peaks), 3.98 (2 H, dd, $J_{PH} = J_{HH} = 7$ Hz) (collapses to d, J_{PH} 7 Hz with D_2O), 2.97 (2 H, d, J_{PH} 20 Hz), 2.35 br (1 H, NH), 2.27 (6 H, 2 or 3 overlapping lines), and 1.40 (9 H, s) (Found: C, 69.25; H, 8.1; N, 4.1. $C_{20}H_{28}NO_2P$ requires C, 69.5; H, 8.2; N, 4.1%). This compound, like the phosphinic ester (**15**; R = Bu^t), decomposed on GLC.

With isopropoxide. The crude product was extracted with ether, leaving the relatively insoluble amide (**16**). The ether extract was diluted with light petroleum, washed thoroughly with water, and concentrated to a small volume; with time

crystals of *isopropyl* N,P-*bis*(4-*methylbenzene*)*phosphonamidate* (**14**; R = Pr^i) were obtained, R_t 7.7 min, m.p. 82–84 °C; *m/z* 331 (M^+, 20%), 288 ($M^+ - C_3H_7$, 60), 184 (20), 120 ($ArCH_2NH^+$, 85), and 105 ($ArCH_2^+$, 100); ν_{max} 3 210 cm^{-1} (NH); $\delta_p(CDCl_3)$ 28.9, $\delta(CDCl_3)$ 7.02 (8 H, s), 4.65 (1 H, d × septet, $J_{PH} \sim J_{HH} \sim 6$ Hz, $OCHMe_2$), 3.94 (2 H, dd, $J_{PH} \sim J_{HH} \sim 6$ Hz, $NHCH_2Ar$), 3.03 (2 H, d, J_{PH} 20 Hz), 2.5 br (1 H, NH), 2.25 (6 H, 2 or 3 overlapping lines), 1.25 (3 H, d, J_{HH} 6 Hz), and 1.18 (3 H, d, J_{HH} 6 Hz) (Found: M^+, 331.1735. $C_{19}H_{26}NO_2P$ requires *M*, 331.1701).

With ethoxide. The phosphinic amide (**16**) was separated as above. The ether extract was then chromatographed on a layer of alumina (eluant 3% ethanol in ether) to give the phosphonamidate (**14**; R = Et), R_F 0.5.

With methoxide. The crude product was chromatographed on a layer of alumina (eluant 2% methanol in ether) to give the phosphonamidate (**14**; R = Me), R_F 0.35; the phosphinic ester (**15**; R = Me), R_F 0.4 and phosphinic amide (**16**), R_F 0.1 were also isolated.

Control Experiments.—(a) Sodium methoxide was added to a solution of the methanesulphonate (**9**) in methanol (temp. ~ 10 °C), causing the signal δ_p 47.5 to be replaced by a signal δ_p 45.8. After 1–2 min the methoxide was neutralised (AcOH); the spectrum then consisted largely of δ_p 47.3. The solvent was evaporated and the residue was extracted with hot benzene. The extract, on cooling, deposited crystals of unchanged (**9**).

(b) A solution of the *N*-methoxyphosphinic amide (**11**) in methanolic sodium methoxide (~0.4M) showed no change (δ_p 47.4) in 70 min. The methoxide was neutralised (AcOH) and the solvent evaporated. The residue was extracted with light petroleum–dichloromethane, and gave unchanged (**11**).

(c) When dissolved in methanolic sodium methoxide (~0.4M) the phosphinoylhydroxylamine (**8**) (δ_p 50.3 in neutral MeOH) was immediately transformed into a compound with δ_p 58.9. This decomposed over 10 min to give mainly sodium bis(4-methylbenzyl)phosphinate (δ_p 34.1; 70%) (isolated and characterised as the free acid, after addition of HCl); the two minor products were tentatively identified as the phosphinic ester (**15**; R = Me) (δ_p 52.3; 25%) and the phosphinic amide (**16**) (δ_p 40.8; 5%). Analogous experiments with ethoxide and isopropoxide gave the sodium phosphinate and phosphinic amide in ratios of 6:1 and 4:1 respectively, with little or none of the phosphinic ester.

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