Rearrangement Reactions of *N*-Phosphinoyl-*O*-sulphonylhydroxylamines with Amines under Competitive Conditions. Possible Involvement of Monomeric Metaphosphonimidates and Phosphonamidic Sulphonic Mixed Anhydrides

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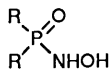
The *O*-methylsulphonyl-*N*-phosphinoylhydroxylamines, RPhP(O)NHOMs (R = Ph, Me, Et, Pr^i), react with an excess of an equimolar mixture of isopropylamine and t-butylamine to give the rearrangement products RP(O)(NHPh)(NHPr^i) and RP(O)(NHPh)(NHBu^t). In the absence of solvent, there is little discrimination between the competing amines (NHPr^i/NHBu^t product ratio 1.45–1.65), as would be expected if rearrangement gave initially a reactive monomeric metaphosphonimidate. However, use of a diluent (CH_2Cl_2) greatly increases the selectivity, implying that much of the initial metaphosphonimidate does not go directly to product. Instead, it seems to recombine with the sulphonate anion to form a phosphonamidic sulphonic mixed anhydride. The observed rearrangement products could then result from reaction of the mixed anhydride with the amines. This may proceed with high selectivity by an $S_N2(P)$ mechanism, or with low selectivity by a preassociative elimination–addition mechanism.

Although *N*-phosphinoylhydroxylamines (**1**) are formally related to hydroxamic acids (**2**), their behaviour differs markedly in some respects, *e.g.* they do not form stable salts in alkaline solution, but rapidly decompose.[1] An important property of



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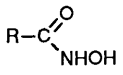
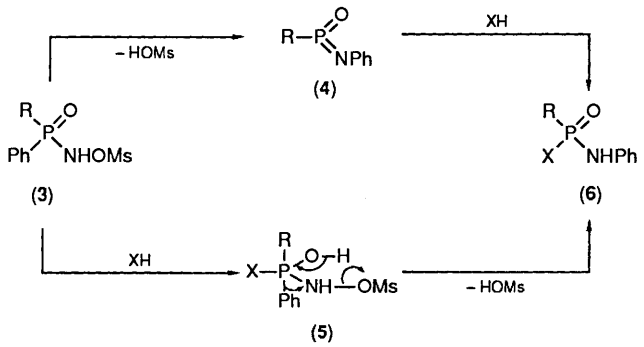


(2)

hydroxamic acids is their ability to form *O*-acyl derivatives that rearrange when treated with base. This is the well-known Lossen rearrangement.[2] Superficially, *N*-phosphinoylhydroxylamines behave in a similar way, *e.g.* the *O*-methylsulphonyl derivative (**3**; R = Ph or alkyl) reacts readily with methylamine or NaOMe–MeOH to give the rearrangement product (**6**; X = MeNH or MeO) in which a phenyl group has migrated from phosphorus to nitrogen.[3,4] Migration of the alkyl group R in (**3**) seems not to be competitive.[4]

Given the formation (and isolation) of isocyanates in the Lossen rearrangement,[2,5] it is tempting to assume that the product (**6**) is derived from the formally analogous monomeric metaphosphonimidate (**4**) (Scheme 1). Like monomeric



Scheme 1.

metaphosphate,[6] this contains a 3-co-ordinate P^V centre. It would, therefore, be a highly reactive electrophile,[7] and in the absence of a suitable trap it would dimerise or polymerise.[8] There can be no prospect of observing it directly, and evidence for its involvement can only be indirect. Such evidence might include a lack of discrimination between competing nucleophiles. We have, therefore, examined the rearrangement of the methanesulphonates (**3**) in the presence of mixtures of amines, chosen so that they differ in nucleophilicity by virtue of their differing degrees of steric hindrance.

Results and Discussion

The methanesulphonates (**3**; R = Ph, Me, Et, or Pr^i) all reacted rapidly when added to an equimolar mixture of isopropylamine and t-butylamine (no additional solvent) at 0 °C. The products were analysed by ^{31}P NMR spectroscopy, with the aid of fully characterised samples of the individual rearrangement products (**6**; X = NHPr^i) and (**6**; X = NHBu^t). In each case, peaks corresponding to both products were seen, the NHPr^i/NHBu^t ratio being in the range 1.45–1.65:1. In contrast, $Ph_2P(O)Cl$ under the same conditions gave almost entirely (*ca.* 99%) the product derived from the more nucleophilic (less hindered) isopropylamine. The low level of discrimination in the rearrangement reactions is consistent with a highly reactive and sterically accessible 3-co-ordinate P^V intermediate—a metaphosphonimidate—being the product-forming species.[9] With other pairs of amines, including $MeNH_2$–$EtNH_2$, $MeNH_2$–Pr^iNH_2, $EtNH_2$–Pr^iNH_2, $EtNH_2$–Bu^tNH_2, and Et_2NH–Bu^tNH_2, the methanesulphonate (**3**; R = Ph) again displayed a rather small preference (< 3-fold) for the less hindered nucleophile. As further evidence of a reactive intermediate, it was found that the methanesulphonate (in CH_2Cl_2) was rapidly converted into (**6**; X = NPr^i_2) with the weakly nucleophilic (highly hindered) di-isopropylamine, whereas $Ph_2P(O)Cl$ did not react at all. Also, in t-butyl alcohol[10] it was converted quantitatively into (**6**; X = OBu^t) when 1 mol equiv. of base (KOBu^t or 2,2,6,6-tetramethylpiperidine) was added.

In spite of this, a very different picture emerged when the Pr^iNH_2–Bu^tNH_2 competitive reactions were repeated using a diluent. In the Table are shown the product ratios obtained using a 20-fold excess of the amine mixture diluted to 1.0, 0.2, or 0.05M total amine concentration with dichloromethane. The reactions clearly become more discriminating, and in suf-

Table. Reactions of *O*-sulphonyl-*N*-phosphinoylhydroxylamines with equimolar mixtures of Pr^iNH_2–Bu^tNH_2 and $MeNH_2$–Bu^tNH_2. Ratios of rearrangement products (**6**) using neat amines and dichloromethane solutions (1.0, 0.2, and 0.05M total amine) at 0 °C.[a]

Reactant	NHPr^i/NHBu^t				NHMe/NHBu^t	
	Neat	1.0M	0.2M	0.05M	Neat	1.0M
(3; R = Ph)	1.55	3.6	25	⩾100	5.9	⩾50
(11)	1.3	1.65	2.95	9.0	2.5	4.4[b]
(3; R = Me)	1.6	7.5	35	(⩾100)[c]	5.0	⩾100
(3; R = Et)	1.45	2.6	14	(⩾100)[c]	3.8	30
(3; R = Pr^i)	1.65	1.5	3.5	(15)[c]	4.0	13

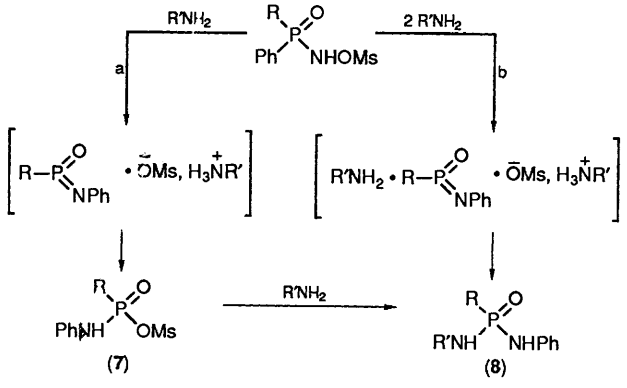
[a] In some of the reactions involving Pr^iNH_2 a substantial amount (0–25%) of the substrate was reduced, without rearrangement, to the amide $PhRP(O)NH_2$. That apart, the rearrangement products were formed in >95% yield (^{31}P NMR spectroscopy) except where otherwise indicated. [b] NHMe/NHBu^t 16.5 at 0.2M; ⩾75 at 0.05M. [c] Substantial amount of unidentified by-product (⩽25%) formed.

ficiently dilute solution can be highly selective. It is difficult to imagine a metaphosphonimidate being stabilised by CH_2Cl_2 to the extent that it becomes highly selective, so some alternative mechanism must apparently be coming into play. An obvious possibility is shown in the lower pathway of Scheme 1, *viz*, nucleophilic attack at phosphorus generates a 5-co-ordinate phosphorane (**5**) which then breaks down with rearrangement. Here the nucleophile attacks associatively at a normal tetrahedral phosphorus, so normal discrimination on steric grounds is to be expected.[11] The observed variations in product ratio would, of course, require the (relatively) unselective metaphosphonimidate mechanism (Scheme 1, top) to be dominant in neat amine, with the selective associative mechanism (Scheme 1, bottom) becoming increasingly important on dilution.

Because of its greater sensitivity to steric effects, the associative mechanism should assume greater prominence if isopropylamine is replaced by methylamine. In accord with this expectation, enhanced selectivity for the less hindered amine was found when the competitive experiments were carried out using a $MeNH_2$–Bu^tNH_2 equimolar mixture (Table).

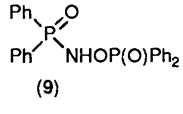
In both sets of competitive experiments, the amount of discrimination tended to decline as the *P*-alkyl group in the substrate was changed from Me to Et to Pr^i. This trend can also be understood in terms of steric effects: the selective associative mechanism would inevitably be disfavoured, relative to the metaphosphonimidate mechanism, by bulky substituents on phosphorus.

For all that, the direction of the changes seen in our experiments accords well with Scheme 1, the magnitude does not. The high sensitivity to steric effects of associative reactions at phosphorus is well documented[11] [pertinent examples include the hydrolyses of PhRP(O)Cl ($k_{Me}:k_{Et}:k_{Pr^i}$ = 750:93:1)[12] and PhRP(O)OMe ($k_{Me}:k_{Ph}$ = 9:1)[13] and the reactions of amines with $Ph_2P(O)Cl$ ($k_{MeNH_2} > 50\ k_{Pr^iNH_2}$ in competitive experiments)], and implies that more dramatic changes should have been observed. More specifically, there are two aspects of relative reactivity that are incompatible with Scheme 1. The first concerns the methanesulphonates (3; R = Me) and (3; R = Pr^i) in their reactions at low amine concentrations. The highly selective nature of the $MeNH_2$–Bu^tNH_2 competitive reactions (Table) would require that both substrates react with $MeNH_2$ at low concentrations by the associative mechanism. The less hindered substrate (R = Me) should, therefore, be much the more reactive. In fact, however, with 0.2M $MeNH_2$ in dichloromethane, the observed rates of reaction are practically identical.[4] The second concerns the reactivity of (3; R = Me) towards $MeNH_2$ and Bu^tNH_2. Even though the competitive experiments at low amine concentrations (⩽ 1M) afford only the product derived from $MeNH_2$, the observed rate of reaction with $MeNH_2$–Bu^tNH_2 (1:1) is not significantly greater than with Bu^tNH_2 alone ($t_{\frac{1}{2}}$ *ca.* 5 and 6 min, respectively, with 0.2M total amine in CH_2Cl_2 at 28 °C). Thus, while $MeNH_2$ is much more effective than Bu^tNH_2 at forming the final product, at inducing reaction of the substrate it is not. The simple associative pathway of Scheme 1 is therefore untenable.* Instead, the selective route to the rearrangement products must involve conversion of the substrate into some intermediate species which *then* experiences nucleophilic attack by amine. We have no conclusive evidence for the identity of the intermediate species, but a phosphonamidic sulphonic mixed anhydride seems likely. Scheme 2 shows in outline how reaction may proceed.



Scheme 2.

(1) If a molecule of amine is already in position when the metaphosphonimidate is formed (preassociation[14]), it can go directly to product (path b), but if not, it combines with the displaced sulphonate anion (and a proton from $R'\overset{+}{N}H_3$) to give the phosphonamidic sulphonic anhydride (7) (path i). A precedent for anhydride formation is provided by the recently observed base-induced rearrangement of *N,O*-bis(diphenylphosphinoyl)hydroxylamine (**9**) to the phosphonamidic phos-



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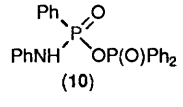


(10)

* It is possible to envisage an associative mechanism involving nucleophilic attack on the substrate at nitrogen rather than phosphorus. However, we would not expect the phosphinic hydrazide that would result to undergo rearrangement, and have confirmed experimentally that $Ph_2P(O)NHNMe_2$ is completely stable under the conditions of our reactions.

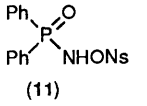
phinic anhydride (**10**).[15] Although the sulphonate anion is only weakly nucleophilic, this will not be a problem if the metaphosphonimidate is a reactive electrophile.[7] Indeed, it is precisely because 3-co-ordinate P^V species such as monomeric metaphosphate are so reactive that they do not often manage to diffuse away from the leaving group, and become fully liberated intermediates, in substitution reactions of P=O compounds.[16,17]

(2) The partitioning of the substrate between the two pathways in Scheme 2 depends on the concentration of amine. Whereas the more direct route to product (path b) is second order in amine (base and nucleophile) and will be favoured by high concentrations, anhydride formation (path a) is first order (base only) and will assume increasing importance on dilution. As regards formation of the product (**8**), the metaphosphonimidate intermediate in the direct route (path b) will discriminate little between competing amines.[18] In contrast, the anhydride, if it reacts by an associative $S_N2(P)$ mechanism, will discriminate strongly in favour of the less hindered amine.[18b] The overall selectivity will, therefore, be small when the direct route predominates (neat amine), but will increase with dilution as the contribution of the selective anhydride route increases.*

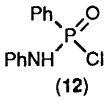
(3) The mixed anhydride (**7**) can react not only with high selectivity by an associative $S_N2(P)$ mechanism, but also with low selectivity by a dissociative elimination–addition (EA) mechanism. In the reactions of the methanesulphonates with 1M amine mixtures, the discrimination against t-butylamine is much greater when the competing amine is methylamine rather than isopropylamine, *e.g.* for (**3**; R = Ph) the product ratios are NHMe/NHBu^t ≥ 50:1 and NHPr^i/NHBu^t = 3.6:1. The high selectivity with $MeNH_2$–Bu^tNH_2 implies that in this case most of the reaction proceeds *via* the mixed anhydride. But isopropylamine can hardly be better than methylamine at trapping the metaphosphonimidate and preventing combination with the sulphonate anion, so most of the Pr^iNH_2–Bu^tNH_2 reaction must also be proceeding *via* the mixed anhydride. Yet the final product ratio now is only 3.6:1. It follows that much of the anhydride must react with Pr^iNH_2–Bu^tNH_2 by a weakly-discriminating EA mechanism. This EA mechanism will be less important in reactions involving methylamine because, being less hindered than isopropylamine, it can attack the anhydride more readily by $S_N2(P)$.

The size of the *P*-alkyl group in the mixed anhydride (**7**) will also influence the way in which it reacts with nucleophiles. Bulky groups retard $S_N2(P)$ but should have little or no effect on the rate of the EA mechanism.[18] The $S_N2(P)$ mechanism should, therefore, decline in importance as R changes Me→Et→Pr^i, and the amine selectivity should decrease accordingly. This is essentially what we observed (Table).

The nature of the sulphonate leaving group in the mixed anhydride could also influence how it reacts with nucleophiles, *i.e.* the better the leaving group, the more important is the dissociative EA mechanism likely to be. The *p*-nitrobenzenesulphonate (**11**) was, therefore, examined. As anticipated, it was found to react with less selectivity than the corresponding methanesulphonate (**3**; R = Ph) in competition experiments (Table).†



(**11**)



(**12**)

(4) In the reactions of the mixed anhydride (**7**) the relative importance of the $S_N2(P)$ and EA mechanisms depends on the amine concentration. Consider, for example, the reactions of the methanesulphonate (**3**; R = Ph) with Pr^iNH_2–Bu^tNH_2 at different concentrations of amine. At 0.05M the NHPr^i/NHBu^t product ratio is ≥100:1. Such high selectivity implies that essentially all the reaction goes *via* the mixed anhydride. At 1.0M the product ratio is only 3.6:1. But even here, as explained above, most of the reaction seems also to go *via* the anhydride. It is, therefore, necessary to postulate that at low amine concentrations the anhydride reacts by the selective $S_N2(P)$ mechanism, but at higher amine concentrations the unselective EA mechanism becomes important.

(5) Phosphonamidic chlorides are useful mechanistic models. Nothing is known about phosphonamidic sulphonic anhydrides but it is reasonable to expect their behaviour to resemble that of phosphonamidic chlorides. The phosphonamidic chloride (**12**)[19] was, therefore, examined as a model for (**7**; R = Ph). It was found to react instantly with Pr^iNH_2–Bu^tNH_2 under competitive conditions to give the product (**8**; R = Ph) having an NHPr^i/NHBu^t ratio of 55:1 with 0.05M amine (CH_2Cl_2 solution), but only 2.3:1 with 1.0M amine. It is, therefore, only at low concentrations of amine that the anhydride pathway in Scheme 2 can be expected to afford a route of high selectivity from the hydroxylamine derivative to the rearrangement product (**8**). The cause of variable selectivity has been established with some certainty for phosphonamidic chlorides.[18b] By extrapolation to phosphonamidic sulphonic anhydrides, it seems likely that the EA mechanism is preassociative and second order in amine (base and nucleophile) whereas the $S_N2(P)$ mechanism is only first order (nucleophile). The relatively unselective EA mechanism is then bound to make a greater contribution at higher concentrations of amine.

Conclusions

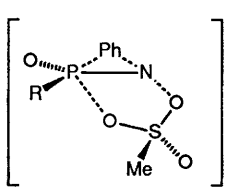
Our results are consistent with the base-induced rearrangement of an *N*-phosphinoyl-*O*-sulphonylhydroxylamine proceeding entirely *via* the metaphosphonimidate (Scheme 2), even when this is clearly not the final product-forming species. By recombining with the sulphonate anion, it can form a phosphonamidic sulphonic mixed anhydride (path a), and with low concentrations of nucleophile (and an inert solvent) this seems to be the dominant process. The final product is then formed by reaction of the mixed anhydride with the nucleophile. This proceeds by both associative [$S_N2(P)$] and dissociative (preassociation elimination–addition) mechanisms, with the partitioning between them, and the product ratio in competitive reactions, depending on the bulk of the substituent on phosphorus, the size of the nucleophile and (presumably) its basicity, the concentration of the base/nucleophile, and the nature of the sulphonate leaving group.

Since the mixed anhydride can react with varying degrees of selectivity it is actually possible to explain the product ratios

* In principle, the phosphonamidic sulphonic anhydride (**7**) could react with R′NH_2 at sulphur instead of phosphorus, giving the phosphonamidic acid R(PhNH)P(O)OH (as its salt with R′NH_2) and the sulphonamide R′NHMs. In a few of our reactions, we observed a ^{31}P NMR signal that might reasonably be attributed to the phosphonamidic acid (and also a very small GLC peak having the same t_R as an authentic sample of the sulphonamide), but the amounts were hardly significant. For phosphoric sulphonic mixed anhydrides attack at phosphorus seems generally to be much preferred, albeit that exceptions have been noted (W. Dabkowski, Z. Skrzypczyński, J. Michalski, N. Piel, L. W. McLaughlin, and F. Cramer, *Nucleic Acids Res.*, 1984, **12**, 9123; W. Dabkowski, J. Michalski, and Z. Skrzypczyński, *Chem. Ber.*, 1985, **118**, 1809; J. Baraniak and W. J. Stec, *J. Chem. Soc., Perkin Trans. 1*, 1987, 1645; and references cited in these).

† It is, of course, conceivable that the lower selectivity observed with the *p*-nitrobenzenesulphonate results in part from less of its rearrangement proceeding *via* the mixed anhydride (path a in Scheme 2).

found in the competition experiments entirely in terms of path i in Scheme 2. It would not seem reasonable to exclude path ii if the sulphonate group becomes completely detached, and the metaphosphonimidate fully formed, when the phenyl group migrates from phosphorus to nitrogen. But if the sulphonate begins to bond to the P atom before its bond to the N atom is completely severed, all of the rearrangement could be directed to the anhydride, *via* a transition state such as (**13**).



(13)

Experimental

Instrumentation generally was as previously described.[20] ^{31}P NMR spectra (^{1}H decoupled) were recorded at 24.3 MHz with a JEOL JNM-FX60 spectrometer; positive chemical shifts are downfield from external 85% H_3PO_4. Light petroleum refers to the fraction b.p. 60–80 °C. Ether refers to diethyl ether. Dichloromethane was distilled from calcium hydride. The amines were dried over KOH and distilled. The *O*-sulphonyl-*N*-phosphinoylhydroxylamines (**3**; R = Ph, Me, Et, Pr^i) and (**11**) were prepared as before.[3,4,21]

Preparative Reactions with Amines.—(*a*) The *O*-methylsulphonyl-*N*-phosphinoylhydroxylamine (**3**; R = Ph, Me, Et, or Pr^i) was mixed with a large excess of the appropriate amine (neat or diluted with CH_2Cl_2). Reaction often occurred immediately and was always complete within a few minutes, except in those cases where the substrate was particularly insoluble in the reaction medium. After examination by NMR spectroscopy (^{1}H and/or ^{31}P), the crude product was dissolved in dichloromethane and washed with a small volume of water (to remove amine salts). The solution was dried, the solvent evaporated, and the product isolated by crystallisation. In the reactions with isopropylamine, the rearrangement product was accompanied by the phosphinic amide $RPhP(O)NH_2$, detected (with the aid of an authentic sample) by ^{31}P NMR spectroscopy [$\delta_P(CH_2Cl_2$–Pr^{i}NH$_2$) 20.6 (R = Ph), 29.0 (Me), 33.3 (Et), 37.4 (Pr^i)] and GLC (3% OV17). Much of this amide was removed by water washing, the rest by crystallisation. In one case (R = Me), the phosphinic amide[22] was isolated and fully characterised. The following phosphonic diamides were prepared.

(**6**; R = Ph, X = NHPr^i), crystallised from chloroform–ether, m.p. 131–132 °C; *m/z* 274 (M^+, 65%), 259 (25, M^+ − Me), and 93 (100, $PhNH_2^+$); δ($CDCl_3$ + D_2O) 8.0–7.3 (5 H, m), 7.2–6.7 (5 H, m), 3.52 (1 H, d × septet, J_{PH} ~ J_{HH} ~ 6 Hz), and 1.13 (6 H, d, J_{HH} 6 Hz) (Found: C, 65.2; H, 6.9; N, 9.8. $C_{15}H_{19}N_2OP$ requires C, 65.7; H, 7.0; N, 10.2%).

(**6**; R = Me, X = NHPr^i), crystallised from ether–light petroleum, m.p. 72–73 °C (softens at 55 °C); *m/z* 212 (M^+, 100%), 197 (55), and 93 (100); δ($CDCl_3$) 7.25–6.7 (5 H, m), 5.65 (1 H, d, J_{PH} 7 Hz, NH), 3.43 (1 H, m), 2.60 (1 H, dd, J_{PH} ~ J_{HH} ~ 9 Hz, NH), 1.54 (3 H, d, J_{PH} 15 Hz), 1.14 and 1.09 (both 3 H, d, J_{HH} 6.5 Hz) (Found: C, 56.7; H, 8.0; N, 13.2. $C_{10}H_{17}N_2OP$ requires C, 56.6; H, 8.1; N, 13.2%).

(**6**; R = Et, X = NHPr^i), crystallised from dichloromethane–light petroleum, m.p. 107.5–108.5 °C; *m/z* 226 (M^+, 80%), 211 (50), and 93 (100); δ($CDCl_3$) 7.3–6.75 (5 H, m), 5.60 (1 H, d, J_{PH} 8 Hz, NH), 3.46 (1 H, m), 2.53 (1 H, dd, J_{PH} ~ J_{HH} ~ 9 Hz, NH), 1.81 (2 H, dq, J_{PH} 15 and J_{HH} 7.5 Hz), 1.13 (3 H, dt, J_{PH} 19 and J_{HH} 7.5 Hz), 1.15 and 1.09 (both 3 H, d, J_{HH} 6.5 Hz) (Found: C, 58.8; H, 8.45; N, 12.2. $C_{11}H_{19}N_2OP$ requires C, 58.4; H, 8.5; N, 12.4%).

(**6**; R = Pr^i, X = NHPr^i), crystallised from dichloromethane–light petroleum, m.p. 127–128 °C; *m/z* 240 (M^+, 80%), 225 (25), and 93 (100); δ($CDCl_3$) 7.3–6.75 (5 H, m), 5.23 (1 H, d, J_{PH} 8 Hz, NH), 3.51 (1 H, m), 2.36 (1 H, dd, J_{PH} ~ J_{HH} ~ 9 Hz, NH), 2.02 (1 H, m), 1.18 and 1.14 (both 3 H, dd, J_{PH} 17.5 and J_{HH} 7 Hz), and 1.16 and 1.10 (both 3 H, d, J_{HH} 7 Hz) (Found: C, 60.1; H, 8.7; N, 11.6. $C_{12}H_{21}N_2OP$ requires C, 60.0; H, 8.8; N, 11.7%).

(**6**; R = Ph, X = NHMe), crystallised from chloroform–ether, m.p. 156–158 °C; *m/z* 246 (M^+, 75%) and 93 (100); δ($CDCl_3$) 8.0–7.3 (5 H, m), 7.2–6.8 (5 H, m), 5.57 (1 H, d, J_{PH} 8 Hz, NH), 3.05 (1 H, br, NH), and 2.61 (3 H, dd, J_{PH} 12 and J_{HH} 6 Hz) (Found: C, 63.2; H, 6.1; N, 11.4. $C_{13}H_{15}N_2OP$ requires C, 63.4; H, 6.2; N, 11.4%).

(**6**; R = Ph, X = NHEt), crystallised from chloroform–ether, m.p. 138–140 °C (lit.,[23] 132–134 °C); δ($CDCl_3$ + D_2O) 8.0–7.25 (5 H, m), 7.15–6.7 (5 H, m), 2.98 (2 H, dq, J_{PH} 9 and J_{HH} 7 Hz), and 1.05 (3 H, t, J_{HH} 7 Hz).

(**6**; R = Ph, X = NEt$_2$), crystallised from tetrachloromethane–ether, m.p. 122–124 °C (lit.,[24] 123 °C); δ($CDCl_3$) 7.9–7.3 (5 H, m), 7.3–6.7 (5 H, m), 4.92 (1 H, d, J_{PH} 10 Hz, NH), 3.23 and 3.20 (both 2 H, dq, J_{PH} ~ J_{HH} ~ 6–7 Hz), and 1.01 (6 H, t, J_{HH} 7 Hz).

(**6**; R = Ph, X = NPr$^i_2$), crystallised from light petroleum, m.p. 175–176 °C; *m/z* 316 (M^+, 16%), 301 (30, M^+ − Me; *m** 286), 273 (20, M^+ − Pr^i; *m** 236), and 86 (100); δ($CDCl_3$) 7.95–7.3 (5 H, m), 7.2–6.7 (5 H, m), 4.86 (1 H, d, J_{PH} 10 Hz, NH), 3.47 (2 H, d × septet, J_{PH} 18 and J_{HH} 7 Hz), and 1.19 and 1.08 (both 6 H, d, J_{HH} 7 Hz) (Found: C, 67.8; H, 7.85; N, 8.65. $C_{18}H_{25}N_2OP$ requires C, 68.3; H, 8.0; N, 8.9%).

The similar preparations and characterisation of (**6**; R = Ph, Me, Et, Pr^i, X = NHBu^t) and (**6**; R = Me, Et, Pr^i, X = NHMe) were reported earlier.[3,4]

Competitive Reactions with Amines.—A suspension of the *O*-sulphonyl-*N*-phosphinoylhydroxylamine (**3**) or (**11**) (0.06 mmol) in dichloromethane (1.1 or 5.9 or 23.9 ml) was stirred magnetically at *ca.* 0 °C and a 20-fold excess (1.2 mmol) of an equimolar mixture of MeNH$_2$–Bu^{t}NH$_2$ (90 μl) or Pr^{i}NH$_2$–Bu^{t}NH$_2$ (113 μl) was added rapidly by syringe. Reaction was allowed to continue at 0 °C for 1 h (1.0M amine) or 24 h (0.2M) or 45 h (0.05M), although it appeared to be complete in a shorter time. Reactions were also performed without any solvent, using a very large excess (*ca.* 0.6 ml) of the amine mixture and a reaction time of 0.5 h. Volatile material was evaporated at room temperature and the crude product was dissolved in dichloromethane and analysed (in duplicate at least) by ^{31}P NMR spectroscopy. The products (**6**) had δ_P 17.1 (R = Ph, X = NHMe), 13.9 (Ph, NHPr^i), 12.1 (Ph, NHBu^t), 25.2 (Me, NHMe), 21.6 (Me, NHPr^i), 19.6 (Me, NHBu^t), 30.1 (Et, NHMe), 26.5 (Et, NHPr^i), 24.7 (Et, NHBu^t), 32.7 (Pr^i, NHMe), 29.4 (Pr^i, NHPr^i), 27.8 (Pr^i, NHBu^t), and were present in the ratios shown in the Table. [The chemical shifts are average values; they refer to crude reaction mixtures and varied somewhat (± 0.5 ppm) between samples]. Some phosphinic amide $RPhP(O)NH_2$ was formed in most of the reactions involving Pr^{i}NH$_2$ (*cf.* preparative reactions above).

Competitive reactions were also carried out using (**3**; R = Ph) and the following pairs of amines: MeNH$_2$–EtNH$_2$; MeNH$_2$–Pr^{i}NH$_2$; EtNH$_2$–Pr^{i}NH$_2$; EtNH$_2$–Bu^{t}NH$_2$; Et$_2$NH–Bu^{t}NH$_2$. In each case ^{1}H NMR spectroscopy was used to establish the presence of both possible products (**6**) (ratio < 3:1), but the reactions were not studied in detail.

For comparison with the results obtained above, competitive reactions were carried out using diphenylphosphinic chloride and pairs of amines (large excess, no solvent); the most significant results are shown below.

Pr^iNH_2–Bu^tNH_2; 98.8% $Ph_2P(O)NHPr^i$ (GLC, 3% OV 17 at 230 °C).

$MeNH_2$–Bu^tNH_2; >99.5% $Ph_2P(O)NHMe$ (GLC, 3% OV 17 at 230 °C).

$MeNH_2$–Pr^iNH_2; >98% $Ph_2P(O)NHMe$ (^{31}P NMR).

t-Butyl N,P-*Diphenylphosphonamidate* (**6**; R = Ph, X = OBu^t).—Potassium t-butoxide (74 mg, 0.66 mmol) was added to a stirred suspension of (**3**; R = Ph) (0.20 g, 0.64 mmol) in t-butyl alcohol (2 ml). After 0.5 h the ^{31}P NMR spectrum consisted of a single peak (δ_P 11.1). The mixture was evaporated to dryness and the residue was partitioned between dichloromethane and water. The organic layer was dried and concentrated. Crystallisation from chloroform–light petroleum afforded the *phosphonamidate* (**6**; R = Ph, X = OBu^t) (64%), m.p. 124 °C (decomp.); *m/z* 289 (M^+, 8%) and 233 (100, $M^+ - C_4H_8$); $\delta(CDCl_3)$ 7.9–6.6 (11 H, includes NH) and 1.58 (9 H, s) (Found: C, 66.45; H, 7.0; N, 4.8. $C_{16}H_{20}NO_2P$ requires C, 66.4; H, 7.0; N, 4.8%). This product was also prepared using 2,2,6,6-tetramethylpiperidine (1 mol equiv.) in place of potassium t-butoxide.

N,N-*Di-isopropyl*-P,P-*diphenylphosphinic Amide*.—Chlorodiphenylphosphine (0.50 g, 2.3 mmol) was added to a stirred solution of di-isopropylamine (0.80 g, 7.9 mmol) in dichloromethane (3 ml). After 0.5 h, the mixture was evaporated to dryness. The residue was dissolved in dichloromethane (5 ml) and oxidised by dropwise addition of sulphuryl chloride (0.31 g, 2.3 mmol). Volatile material was evaporated and the residue was partitioned between chloroform and water. The organic layer was dried. Crystallisation from light petroleum containing a little chloroform gave the *phosphinic amide* (81%), m.p. 118–119 °C; *m/z* 301 (M^+, 2%), 286 (30, M^+ – Me), 258 (25), 244 (35), and 201 (100, $M^+ - NPr^i_2$); $\delta(CDCl_3)$ 7.9–7.2 (10 H, m), 3.43 (2 H, d × septet, J_{PH} 16 and J_{HH} 7 Hz), and 1.20 (12 H, d, J_{HH} 7 Hz) (Found: C, 71.9; H, 8.1; N, 4.4. $C_{18}H_{24}NOP$ requires C, 71.7; H, 8.0; N, 4.65%). This compound could not be prepared from diphenylphosphinic chloride and di-isopropylamine (with or without a solvent).

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