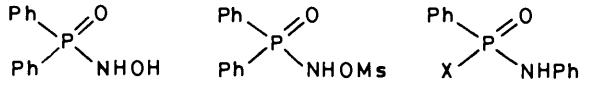
N-(Alkylphenylphosphinoyl)hydroxylamines: Highly Selective Migration of the Phenyl Group in the Base-induced Rearrangement of their *O*-Methylsulphonyl Derivatives[1]

Martin J. P. Harger* and Adrian Smith
Department of Chemistry, The University, Leicester LE1 7RH

The *N*-(alkylphenylphosphinoyl)hydroxylamines RPh(O)NHOH (R = Me, Et, or Pr^i) have been prepared and converted into their *O*-methylsulphonyl derivatives RPhP(O)NHOMs. These readily rearrange on treatment with methylamine, t-butylamine, or sodium methoxide–methanol to give only the products RP(O)(NHPh)X (X = NHMe, NHBu^t, or OMe) resulting from migration of the phenyl group. The rates of reaction are essentially the same when R = Me and R = Pr^i, indicating that rearrangement is not brought about by nucleophilic attack at phosphorus. A likely mechanism involves base-induced rearrangement to a monomeric metaphosphonimidate which then reacts rapidly with the nucleophile.

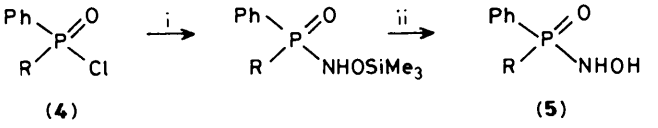
N-Phosphinoylhydroxylamines such as (**1**) are the phosphorus analogues of hydroxamic acids (RCONHOH). The first examples were prepared only fairly recently,[2] and were found to undergo Lossen-like[3] rearrangements when suitably activated. Thus, for example, when the *O*-methanesulphonate (**2**) was treated with t-butylamine or sodium methoxide–methanol a phenyl group migrated from phosphorus to nitrogen and (**3**; X = Bu^{t}NH) or (**3**; X = MeO) was produced in high yield.[2] To extend the scope of the rearrangement and to learn more about its mechanism, we have now prepared some unsymmetrical analogues of (**1**) and (**2**) in which one of the phenyl groups is replaced by an alkyl group.



(**1**) (**2**) (**3**)

Results and Discussion

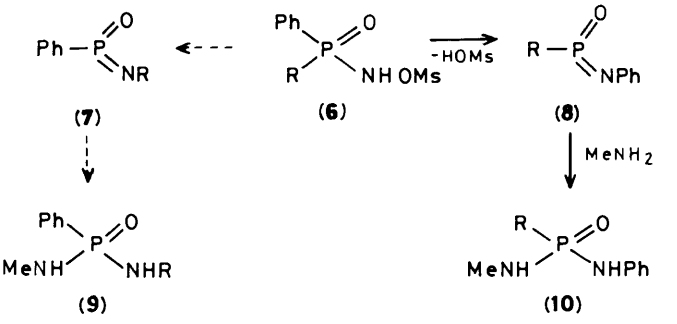
The *N*-(alkylphenylphosphinoyl)hydroxylamines (**5**; R = Me, Et, or Pr^i) were prepared from the phosphinic chlorides (**4**) using *O*-trimethylsilylhydroxylamine (Scheme 1). They proved



(**4**) (**5**)

Scheme 1. *Reagents:* i, $H_2NOSiMe_3$, Et_3N; ii, MeOH

to be solids of limited stability, decomposing at or below the m.p. [one sample of (**5**; R = Me) decomposed vigorously without melting after several hours at warm room temperature], but they were obtained essentially pure by careful crystallisation and could be stored for weeks at −20 °C without deterioration. Unfortunately it was not possible to complete the series with the t-butyl compound because steric hindrance prevented the phosphinic chloride (**4**; R = Bu^t) from reacting with *O*-trimethylsilylhydroxylamine. With methanesulphonyl chloride in pyridine at 0 °C, the hydroxylamines were converted into crystalline *O*-methylsulphonyl derivatives (**6**; R = Me, Et, or Pr^i). These also melted with decomposition but were sufficiently stable to give molecular ions in electron-impact mass spectrometry. The most striking feature of their ^{1}H n.m.r. spectra was the NH signal. In dimethyl sulphoxide (DMSO) this appeared at low field (δ 10.5—10.2) as a sharp phosphorus-coupled doublet (J_{PH} 7—9 Hz).

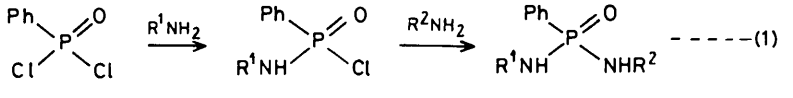


Scheme 2.

The methanesulphonates (**6**) reacted vigorously when treated with an excess of anhydrous liquid methylamine (b.p. −6.5 °C). In each case the ^{31}P n.m.r. spectrum of the crude product was seen to be dominated by a single peak [$\delta_P(CH_2Cl_2)$ 25.0, 29.9, or 32.5 for R = Me, Et, or Pr^i respectively]† accounting for at least 98% of the total spectrum. The product was isolated by crystallisation and was characterised as the *P*-alkyl-*N*-methyl-*N*′-phenylphosphonic diamide (**10**) resulting from migration of the phenyl group. Evidence for the phenyl group being on N rather than P was seen in the ^{1}H n.m.r. spectrum, where its signals appeared at δ 7.3—6.7 (m) and the characteristic PhP(O) pattern at δ 8.0—7.25 was absent, and where the two P–coupled NH signals had very different chemical shifts (δ 6—5, NHPh; δ 3—2, NHMe), and also in the mass spectrum where *m*/*z* 93 ($H_2\overset{+\cdot}{N}Ph$) was the most abundant ion. That the alkyl group R was still attached directly to P was clear from the chemical shifts of its protons and/or the size of the couplings to phosphorus ($J_{PH} \geqslant 12$ Hz for all the protons in R). There was no evidence for the alternative rearrangement product (**9**) resulting from alkyl migration, although only in the case where R = Me could an authentic sample be prepared [$PhP(O)Cl_2$ + excess $MeNH_2$; $\delta_P(CH_2Cl_2)$ 23.6] and its absence from the crude

† Quoted values of the ^{31}P n.m.r. chemical shift δ_P relate to isolated and purified compounds; in reaction mixtures (containing an excess of amine *etc.*) the values of δ_P sometimes differed by as much as 1 p.p.m.

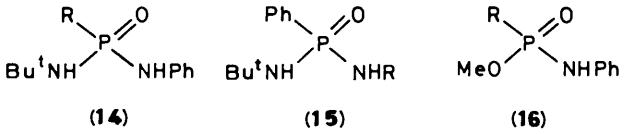
product be established beyond doubt (1% would have been detected by ^{31}P n.m.r. spectroscopy). In principle, authentic samples of (**9**; R = Et or Pr^i) should have been available from phenylphosphonic dichloride by sequential replacement of the chlorine atoms (Scheme 3), but in our experience phosphonamidic chlorides (**12**) derived from primary aliphatic amines are not generally stable. Exceptionally, t-butylamine derivatives are often stable,[4] and (**12**; R^1 = Bu^t) can be prepared and isolated. We therefore examined the reactions of the methanesulphonates (**6**) with t-butylamine, having first made use of (**12**; R^1 = Bu^t) to obtain authentic samples of the alkyl-migration products (**15**). With the aid of these samples it was possible to show by g.l.c. (or ^{31}P n.m.r. spectroscopy) that migration of the alkyl group accounted for at most 0.5% of the products resulting from the methanesulphonate rearrangements. The products (**14**) resulting from phenyl migration were formed quantitatively (^{31}P n.m.r. spectroscopy), and were easily isolated and characterised.



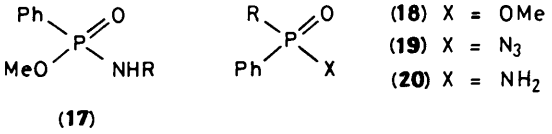
(**11**) (**12**) (**13**)

Scheme 3.

The methanesulphonates (**6**) also rearranged very rapidly when sodium methoxide (2 mol equiv.) was added to suspensions in methanol. Here too the products (**16**) were those resulting from phenyl migration, with none of the alkyl-migration products (**17**) being observed ($\leqslant$0.2% would have been detected by g.l.c. for R = Et or Pr^i, $\leqslant$1% by ^1H n.m.r. for R = Me). There were, however, small amounts of the methyl phosphinates (**18**) (0.3—10%), formed presumably by nucleophilic attack at phosphorus in the substrate.



(**14**) (**15**) (**16**)



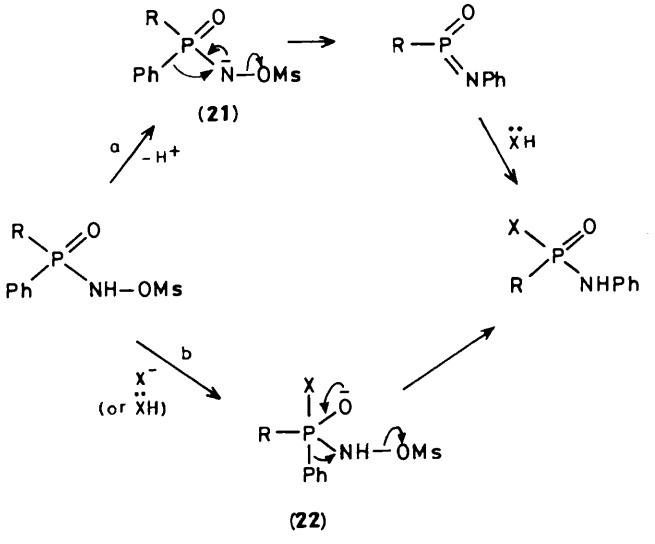
(**17**)

(**18**) X = OMe
(**19**) X = N_3
(**20**) X = NH_2

Exclusive migration of the phenyl group in these rearrangements is at first sight rather surprising, albeit that it makes them the more attractive for use in preparative work. Direct (competitive) comparison of migrating groups is not, of course, possible with hydroxamic acid (RCONHOH) derivatives, but kinetic measurements suggest that alkyl groups (except perhaps Me) migrate just as readily as phenyl in Lossen rearrangements.[5] Indeed, the rearrangement of RCONOCOPh is 11.5 times faster when the migrating group R is cyclohexyl as opposed to phenyl.[5a] The most directly related reaction we know of is the photochemical Curtius-like rearrangement of phosphinic azides, and in methanol the azides (**19**) form both of the possible rearrangement products (**16**) and (**17**).[6] What is more, such discrimination as there is favours alkyl, not phenyl, migration: the migration ratios (R:Ph) are 2.1:1 (R = Bu^t), 1.7:1 (R = Pr^i), 1.3:1 (R = Et), and 1.2:1 (R = Me).[6] These reactions are, however, less clean than the Lossen-like rearrangements and give some products, including the phosphinic amides (**20**), suggestive of nitrene intermediates.[6,7] If the azides rearrange *via* highly reactive nitrenes, it is not unreasonable that they should show relatively little discrimination between different migrating groups. And even if a nitrene is not involved in the rearrangement, the species that does rearrange will presumably be some high energy (low selectivity) excited state of the azide. For the methanesulphonate rearrangements, on the other hand, the mild conditions, the cleanness of the reactions [including the absence of the amides (**20**) in the reactions in methanol], and the high discrimination between phenyl and alkyl migrating groups suggest that they probably follow a non-nitrene mechanism.

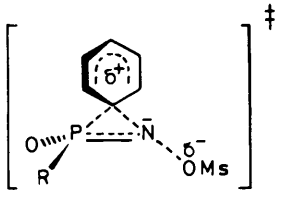
An obvious possibility, given that hydroxamic acid derivatives form isocyanates in the Lossen rearrangement,[3,8] involves loss of the sulphonate anion from the conjugate base (**21**) and simultaneous migration of a group from P to N (Scheme 4, path a). The resulting monomeric metaphosphonimidate would contain three-co-ordinate P^V and, like monomeric metaphosphate,[9] would react very quickly with a nucleophile (XH) such as MeOH or $MeNH_2$.[9] There is, however, an attractive alternative mechanism that does not involve a metaphosphonimidate. In this the first step would be nucleophilic attack at phosphorus to give a phosphorane (**22**) which could then break down as shown (Scheme 4, path b). In a phosphorane there are distinct apical and equatorial positions. If migration were possible from only one of these, and phenyl, but not alkyl, was in the correct position, the exclusive migration of the phenyl group could easily be rationalised. Since our original objective in studying phosphinoylhydroxylamines had been to find a gentle non-photochemical route to monomeric metaphosphonimidates, we were much concerned to distinguish between these possible mechanisms. This we sought to do by comparing the rates of reaction of the methanesulphonates (**6**) having R = Me and R = Pr^i. A mixture of comparable amounts of the two substrates (*ca.* 10 mg each) dissolved in dichloromethane (1.1 ml) (the compounds have rather low solubilities) was placed in the probe of the ^{31}P n.m.r. spectrometer. To this was added an excess of methylamine (*ca.* 5.5 mol equiv., giving *ca.* 0.2M solution), causing the peaks due to the substrates to be replaced during 1 h by those due to the rearrangement products ($t_{\frac{1}{2}}$ *ca.* 8 min at 20 °C). Significantly, the product ratio (**10**; R = Me):(**10**; R = Pr^i) remained constant throughout, and equal to the substrate ratio (**6**; R = Me):(**6**; R = Pr^i), showing that the substrates were reacting at essentially the same rate. With NaOMe–MeOH the reactions were too fast to follow satisfactorily. We therefore took advantage of the fact that in this case reaction can be carried out using only a limited amount of base (NaOMe) but with a large excess of nucleophile (MeOH) present to ensure the efficient trapping of any metaphosphonimidates. Thus the two substrates (0.1 mmol of each) were dissolved in methanol (1.1 ml) and were made to compete for sodium methoxide (0.1 mmol). When the base had been consumed, the ^{31}P n.m.r. spectrum of the reaction mixture contained four similar sized peaks, two for the substrates and two for the rearrangement products (**16**; R = Me or Pr^i) showing that *ca.* 50% of each substrate had reacted. Here too there is clearly no significant difference in the rate of reaction of the two substrates. This equal reactivity is not compatible with a mechanism involving initial nucleophilic attack on the substrate (Scheme 4, path b), given the importance of steric effects in such

reactions.[10] Typically, the rates of hydrolysis of $R_2P(O)OMe$ (alkaline solution) and RPhP(O)Cl decrease by factors of 1 650 and 750 respectively when R is changed from methyl to isopropyl.[11] Equal substrate reactivity is, however, entirely reasonable for a mechanism in which the reagent acts initially as a base (Scheme 4, path a), and nucleophilic attack at phosphorus occurs only after rearrangement has produced a highly reactive monomeric metaphosphonimidate. Some additional mechanistic evidence comes from the methyl phosphinate by-products (**18**) seen in the original reactions of the methanesulphonates with sodium methoxide in methanol. These esters presumably result from nucleophilic attack at phosphorus. If rearrangement were also proceeding by nucleophilic attack, the proportion of substrate converted into ester would be more or less independent of the nature of the group R. This is not what we found: the yields of ester decreased markedly as R changed from methyl (10%) to ethyl (1.3%) to isopropyl (0.3%), showing that nucleophilic attack declines in importance as the size of R increases.



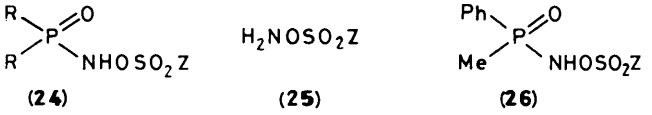
Scheme 4.

Accepting that rearrangement does indeed follow path a in Scheme 4, the very low migration tendency of alkyl groups relative to phenyl remains to be explained. It seems unlikely that the metaphosphonimidates (**7**) and (**8**) differ greatly in stability, yet the transition state leading to (**8**) is clearly much the more favourable. We have recently found that, in comparison with phenyl, migration of p-XC_6H_4 is quite strongly assisted by electron-releasing groups X and inhibited by electron withdrawal.[12] The substituent effects correlate with σ^+ (ρ −1.7) rather than σ and seem to indicate that the π-system of the migrating group is substantially involved in the transition state. Perhaps, then, the absence of alkyl migration in the present study is simply a consequence of the alkyl group having no π electrons with which to form a phenonium ion-like transition state (**23**).



(23)

One would obviously like to know whether alkyl groups can migrate when there is no competition, *i.e.* whether the dialkyl compounds (**24**; Z = Me *etc.*) will undergo rearrangement. Unfortunately our attempts to prepare simple *N*-(dialkylphosphinoyl)hydroxylamines have been unsuccessful. This is not altogether surprising; they are unlikely to be solids and we know that in general phosphinoylhydroxylamines decompose when they melt. We considered the possibility of making the sulphonyl derivatives directly from the phosphinic chlorides and *O*-sulphonylhydroxylamines, but exploratory studies were not encouraging. In these we used *O*-arylsulphonylhydroxylamines (**25**; Z = mesityl or *p*-tolyl)[13,14] rather than the methylsulphonyl compound, because of their greater stability. Also, instead of dialkylphosphinic chlorides we used the methylphenyl compound (**4**; R = Me). This enabled us to have to hand samples of the hoped-for products (**26**; Z = *p*-tolyl or mesityl) made by sulphonylation of the phosphinoylhydroxylamine (**5**; R = Me). Although they were found to be reasonably stable crystalline compounds, attempts to prepare them from the phosphinic chloride and sulphonylhydroxylamines were not successful. At present, therefore, we see little prospect of obtaining the compounds (**24**) and ascertaining whether or not they undergo Lossen-like rearrangements.



(24) (25) (26)

Experimental

Instrumentation was generally as before.[2] Positive ^{31}P n.m.r. chemical shifts are downfield from external 85% H_3PO_4; the values quoted are for isolated and purified compounds, and in some cases differ by *ca.* 1 p.p.m. from the values observed in crude reaction mixtures. I.r. frequencies relate to spectra recorded as Nujol mulls. All the phosphonic diamides gave i.r. spectra with peaks at 3 400—3 100 (NH) and 1 190—1 150 cm^{-1} (P=O). G.l.c. analyses were performed on a Pye 104 flame-ionisation chromatograph fitted with a 1.5m × 4 mm internal diameter glass column packed with the stated stationary phase coated on silanised 100—120 mesh diatomite C 'Q' (on-column injection). Amines were dried over, and distilled from, potassium hydroxide. Light petroleum refers to the fraction with b.p. 60—80 °C. *O*-Trimethylsilylhydroxylamine was prepared as previously described.[2] CAUTION. A sample of *N*-(methylphenylphosphinoyl)hydroxylamine (**5**; R = Me) decomposed vigorously after several hours at warm room temperature. Although this was an isolated incident all the hydroxylamine derivatives described in this paper were treated as potentially unstable (*e.g.* only brief heating during crystallisation; storage at −20 °C).

N-(Methylphenylphosphinoyl)hydroxylamine (**5**; R = Me).—Methylphenylphosphinic chloride[15] (3.3 g, 18.9 mmol) in dichloromethane (19 ml) was added dropwise with stirring over 0.5 h to a mixture of *O*-trimethylsilylhydroxylamine (2.5 g, 23.6 mmol) and triethylamine (2.0 g, 20.0 mmol) dissolved in dichloromethane (36 ml), the temperature being maintained at *ca.* 15 °C by occasional gentle cooling. Some solid (Et_3NHCl) precipitated. After a further 1 h at room temperature desilylation was accomplished by adding methanol (1.75 g, 55 mmol) and leaving the resulting clear solution at room temperature. Solid began to crystallise out after 10 min, and after 1.2 h the crystals were filtered off and washed with dichloromethane, giving the *hydroxylamine* (**5**; R = Me) (2.50 g, 77%), m.p. 74—76 °C (decomp.), $\nu_{max.}$ 3 195 (NHOH), 1 165,

and 1 155 cm^{-1} (P=O); δ(CD_3SOCD_3) 8.0 (1 H, d, J_{PH} 6 Hz), 7.9—7.4 (6 H, m), and 1.53 (3 H, d, J_{PH} 13 Hz). The m.p. was unchanged after crystallisation from methanol–dichloromethane (Found: C, 48.6; H, 5.85; N, 8.2. $C_7H_{10}NO_2P$ requires C, 49.1; H, 5.9; N, 8.2%).

N-(*Ethylphenylphosphinoyl*)*hydroxylamine* (**5**; R = Et).—This was prepared from ethylphenylphosphinic chloride[16] following the above procedure except that before desilylation the reaction mixture was diluted with ether (2 vols) to precipitate Et_3NHCl which was filtered off. Methanol (3 mol equiv.) was then added to the filtrate. Crystallisation of the product was initiated by scratching and continued over 4 h to give the *hydroxylamine* (**5**; R = Et) (54%), m.p. 86—87 °C (decomp.), *m/z* 185 (M^+, 15%); $\nu_{max.}$ 3 190 (NHOH) and 1 150 cm^{-1} (P=O); δ(CD_3SOCD_3) 7.97br (1 H), 7.85—7.30 (6 H, m), 2.1—1.6 (2 H, m), and 0.93 (3 H, dt, J_{PH} 18, J_{HH} 7 Hz), δ_P(CD_3SOCD_3–CH_2Cl_2) 39.9. A sample recrystallised from dichloromethane had m.p. 82.5—83.5 °C (decomp.) (Found: C, 51.6; H, 6.25; N, 7.7. $C_8H_{12}NO_2P$ requires C, 51.9; H, 6.5; N, 7.6%).

N-(*Isopropylphenylphosphinoyl*)*hydroxylamine* (**5**; R = Pr^i).—This was similarly prepared from isopropylphenylphosphinic chloride[16] except that, because the reaction was slower, more concentrated solutions (1.5 fold) were used and reaction was allowed to proceed for 2.5 h. Before desilylation, the reaction mixture was diluted with ether (1.5 vols), filtered (to remove Et_3NHCl), and evaporated. The residue was dissolved in ether (2.5 ml/mmol), methanol (3 mol equiv.) was added, and the solution was kept at room temperature for 1 h and then at 0 °C overnight giving the crude solid hydroxylamine (44%), δ_P(CH_2Cl_2) 45.4 [impurity at 41.4 (12%)]. Recrystallisation from dichloromethane–ether gave the pure *hydroxylamine* (**5**; R = Pr^i), m.p. 114—116 °C (decomp.), $\nu_{max.}$ 3 250, 3 160 (NHOH), and 1 150 cm^{-1} (P=O); δ($CDCl_3$) 7.9—6.6 (7 H; peaks due to Ph superimposed on a broad hump), 2.31 (1 H, d × septet, J_{PH} 14, J_{HH} 7 Hz), 1.13 (3 H, dd, J_{PH} 18, J_{HH} 7 Hz), and 1.04 (3 H, dd, J_{PH} 18, J_{HH} 7 Hz) (Found: C, 54.3; H, 7.0; N, 7.1. $C_9H_{14}NO_2P$ requires C, 54.3; H, 7.1; N, 7.0%).

N-*Phosphinoyl*-O-*sulphonylhydroxylamines*.—(a) A suspension of *N*-(methylphenylphosphinoyl)hydroxylamine (**5**; R = Me) (0.75 g, 4.4 mmol) in cold pyridine (1.8 ml) was mixed thoroughly and cooled in ice while methanesulphonyl chloride (0.56 g, 4.9 mmol) was added. After 5 min most of the pyridine was quickly evaporated under vacuum at 0 °C and the residue was mixed with iced water (20 ml). The crude product was filtered off, washed with water, and dried. It was purified by washing with ether and recrystallising from ethanol–ether (or aqueous methanol) to give N-(*methylphenylphosphinoyl*)-O-*methylsulphonylhydroxylamine* (**6**; R = Me) (0.61 g, 56%), m.p. 77—78 °C (decomp.), *m/z* 249 (M^+, 10%); $\nu_{max.}$ *ca.* 3 000 (shoulder on Nujol, NH) and 1 180 cm^{-1} (P=O); δ(CD_3SOCD_3) 10.24 (1 H, d, J_{PH} 7 Hz), 7.9—7.4 (5 H, m), 3.19 (3 H, s), and 1.76 (3 H, d, J_{PH} 14 Hz) (Found: C, 38.7; H, 4.8; N, 5.8. $C_8H_{12}NO_4PS$ requires C, 38.55; H, 4.85; N, 5.6%).

(b) The following were prepared from the appropriate *N*-phosphinoylhydroxylamines as in (a) except that after collecting the crude product the aqueous filtrate was extracted several times with chloroform. The extracts were evaporated and the residue was triturated with chloroform–ether to give a small additional amount of product.

N-(*Ethylphenylphosphinoyl*)-O-*methylsulphonylhydroxylamine* (**6**; R = Et) (52%), m.p. 108—109 °C (decomp.), *m/z* 263 (M^+, 4%); $\nu_{max.}$ 3 040 (NH) and 1 185 cm^{-1} (P=O); δ(CD_3SOCD_3) 10.32 (1 H, d, J_{PH} 8 Hz), 7.9—7.4 (5 H, m), 3.18 (3 H, s), 2.2—1.8 (2 H, m), and 1.01 (3 H, dd, J_{PH} 18, J_{HH} 8 Hz); δ_P(CD_3SOCD_3–CH_2Cl_2) 40.3 (Found: C, 41.05; H, 5.35; N, 5.3. $C_9H_{14}NO_4PS$ requires C, 41.1; H, 5.4; N, 5.3%).

N-(*Isopropylphenylphosphinoyl*)-O-*methylsulphonylhydroxylamine* (**6**; R = Pr^i) (28%; before recrystallisation, 40%), m.p. 149—150 °C (decomp.), *m/z* 277 (M^+, 30%), $\nu_{max.}$ 3 050 (NH), 1 195, and 1 185 cm^{-1} (P=O); δ(CD_3SOCD_3) 10.53 (1 H, d, J_{PH} 9 Hz), 7.9—7.4 (5 H, m), 3.20 (3 H, s). 2.5—2.0 (1 H, m), 1.18 (3 H, dd, J_{PH} 17, J_{HH} 7 Hz), and 0.91 (3 H, dd, J_{PH} 18, J_{HH} 7 Hz); δ_P(CH_2Cl_2) 45.8 (Found: C, 43.8; H, 5.8; N, 4.8. $C_{10}H_{16}NO_4PS$ requires C, 43.3; H, 5.8; N, 5.05%). In this case the reaction time was increased to 10 min and on quenching with water the product was obtained as an oil that slowly solidified.

(c) *N*-(Methylphenylphosphinoyl)hydroxylamine (**5**; R = Me) was treated with mesitylenesulphonyl chloride as in (a). The crude product formed as an oil, but solidified on trituration with a little methanol. Crystallisation from aqueous methanol afforded N-(*methylphenylphosphinoyl*)-O-*mesitylsulphonylhydroxylamine* (30%), m.p. 85—87 °C (decomp.), $\nu_{max.}$ 3 060 (NH), 1 190, and 1 175 cm^{-1} (P=O); δ($CDCl_3$) 7.8—7.2 (6 H, m), 6.90 (2 H, s), 2.54 (6 H, s), 2.27 (3 H, s), and 1.75 (3 H, d, J_{PH} 15 Hz); δ_P(CH_2Cl_2) 39.9 (Found: C, 54.3; H, 5.7; N, 4.0. $C_{16}H_{20}NO_4PS$ requires C, 54.4; H, 5.7; N, 4.0%).

(d) Toluene-*p*-sulphonyl chloride (1.43 g, 7.5 mmol) and triethylamine (0.73 g, 7.2 mmol) were added in order to a stirred suspension of *N*-(methylphenylphosphinoyl)hydroxylamine (1.28 g, 7.5 mmol) in tetrahydrofuran (80 ml) at room temperature. After 27 h solid (Et_3NHCl) was filtered off, the filtrate concentrated, and the residue crystallised from chloroform–benzene to give *N*-(*methylphenylphosphinoyl*)-O-p-*tolylsulphonylhydroxylamine* (1.46 g, 60%), m.p. 96 °C (decomp.) (after recrystallisation from CH_2Cl_2 at −20 °C); $\nu_{max.}$ *ca.* 3 050 (shoulder on Nujol, NH), 1 200, 1 190, and 1 170 cm^{-1} (P=O); δ($CDCl_3$) 7.9—7.2 (10 H, including 7.58, s, exchanges with D_2O), 2.41 (3 H, s), and 1.66 (3 H, d, J_{PH} 14 Hz) (Found: C, 51.6; H, 4.95; N, 4.3; P, 9.4. $C_{14}H_{16}NO_4PS$ requires C, 51.7; H, 5.0; N, 4.3; P, 9.5%).

Authentic samples of N,N′-*Dialkyl*-P-*phenylphosphonic Diamides*.—The diamides (**15**) were prepared by reaction of *N*-t-butyl-*P*-phenylphosphonamidic chloride[2] with the appropriate amine (≥2 mol equiv.) in dichloromethane. The reaction mixtures were washed with water, evaporated, and the residue crystallised from light petroleum (containing some dichloromethane to increase the solubility). The following were obtained.

N-*Methyl*-P-*phenyl*-N′-*t-butylphosphonic diamide* (**15**; R = Me), m.p. 88.5—90 °C, *m/z* 226 (M^+, 1%) and 211 (100); δ($CDCl_3$) 7.9—7.25 (5 H, m), 2.56 (3 H, d, J_{PH} 11 Hz), *ca.* 2.5br (2 H, NH), and 1.29 (9 H, s) (the d at δ 2.56 was rather broad but sharpened when the NH protons were exchanged with D_2O); δ_P(CH_2Cl_2) 19.2 (Found: C, 58.65; H, 8.5; N, 12.5. $C_{11}H_{19}N_2OP$ requires C, 58.4; H, 8.5; N, 12.4%).

N-*Ethyl*-P-*phenyl*-N′-*t-butylphosphonic diamide* (**15**; R = Et), m.p. 69—70 °C, *m/z* 240 (M^+, 2%) and 225 (100); δ($CDCl_3$) 7.9—7.25 (5 H, m), 2.92 (2 H, ddq, J_{PH}, J_{HH}, J_{HH} all 7—8 Hz), *ca.* 2.4 (2 H, br, NH), 1.28 (9 H, s), and 1.08 (3 H, t, J_{HH} 7 Hz); δ_P(CH_2Cl_2) 16.9 (Found: C, 60.2; H, 8.8; N, 11.8. $C_{12}H_{21}N_2OP$ requires C, 60.0; H, 8.8; N, 11.7%).

N-*Isopropyl*-P-*phenyl*-N′-*t-butylphosphonic diamide* (**15**; R = Pr^i), m.p. 135—136 °C, *m/z* 254 (M^+, 4%), 253 (4), and 239 (100); δ($CDCl_3$) 7.9—7.25 (5 H, m), 3.40 (1 H, m), *ca.* 2.3 (2 H, br, NH), 1.28 (9 H, s), 1.15 (3 H, d, J_{HH} 6 Hz), and 1.04 (3 H, d, J_{HH} 6 Hz); δ_P(CH_2Cl_2) 15.5 (Found: C, 61.6; H, 9.0; N, 10.9. $C_{13}H_{23}N_2OP$ requires C, 61.4; H, 9.1; N, 11.0%).

Reaction of phenylphosphonic dichloride with an excess of methylamine in dichloromethane, followed by washing with water and crystallisation from chloroform–light petroleum, gave *N*,*N*′-dimethyl-*P*-phenylphosphonic diamide (**9**; R = Me),[17] m.p. 105—107 °C, *m/z* 184 (M^+, 80%), 155 (100), and

154 (90); δ($CDCl_3$) 7.9—7.25 (5 H, m), *ca.* 2.5br (2 H, NH), and 2.56 slightly br (6 H, d, J_{PH} 12 Hz); $\delta_P(CH_2Cl_2)$ 23.6.

Reactions of N-(*Alkylphenylphosphinoyl*)-O-*methylsulphonyl hydroxylamines* (**6**).—(a) *With t-butylamine.* The appropriate methanesulphonate (**6**) (0.4 mmol) was mixed with t-butylamine (30—50 mol equiv.) at room temperature. It dissolved (reacted) over 5—10 min (slightly exothermic), and after a further 15 min the excess amine was evaporated. The crude product was dissolved in dichloromethane and was examined by ^{31}P n.m.r. spectroscopy and by g.l.c. (3% OV 17, 215 °C). A single product was observed, and, with the aid of an authentic sample, the absence of the *N*-alkyl-*P*-phenyl-*N'*-t-butylphosphonic diamide (**15**) was established (≤0.5% would have been detected). The solution was washed with water (to remove $Bu^tNH_3OSO_2Me$) and evaporated. The following were obtained.

P-*Methyl*-N-*phenyl*-N'-*t-butylphosponic diamide* (**14**; R = Me), crystallised from chloroform–light petroleum, m.p. 131.5—132.5 °C, *m/z* 226 (M^+, 70%), 211 (M^+ − Me, 90), and 93 ($Ph\overset{+\bullet}{N}H_2$, 60); δ($CDCl_3$) 7.3—6.75 (5 H, m), 5.88 (NH, d, J_{PH} 7 Hz), 2.67 (NH, d, J_{PH} 10 Hz), 1.57 (3 H, d, J_{PH} 15 Hz), and 1.30 (9 H, s); $\delta_P(CH_2Cl_2)$ 19.6 (Found: C, 58.6; H, 8.45; N, 12.4. $C_{11}H_{19}N_2OP$ requires C, 58.4; H, 8.5; N, 12.4%).

P-*Ethyl*-N-*phenyl*-N'-*t-butylphosphonic diamide* (**14**; R = Et), crystallised from ether–light petroleum, m.p. 94.5—95.5 °C, *m/z* 240 (M^+, 50%), 225 (60), and 93 (85); δ($CDCl_3$) 7.3—6.75 (5 H, m), 5.83 (NH, d, J_{PH} 6 Hz), 2.55 (NH, d, J_{PH} 12 Hz), 1.83 (2 H, dq, J_{PH} 14, J_{HH} 7 Hz), 1.30 (9 H, s), and 1.10 (3 H, dt, J_{PH} 19, J_{HH} 7 Hz); $\delta_P(CH_2Cl_2)$ 24.6 (Found: C, 60.2; H, 8.8; N, 11.65. $C_{12}H_{21}N_2OP$ requires C, 60.0; H, 8.8; N, 11.7%).

P-*Isopropyl*-N-*phenyl*-N'-*t-butylphosphonic diamide* (**14**; R = Pr^i), crystallised from dichloromethane–light petroleum, m.p. 153—155 °C, *m/z* 254 (M^+, 70), 239 (65), and 93 (100); δ($CDCl_3$) 7.3—6.7 (5 H, m), 5.26 (NH, d, J_{PH} 7 Hz), 2.37 (NH, d, J_{PH} 13 Hz), 1.99 (1 H, d × septet, J_{PH} 14, J_{HH} 7 Hz), 1.32 (9 H, s), 1.21 (3 H, dd, J_{PH} 17, J_{HH} 7 Hz), and 1.14 (3 H, dd, J_{PH} 17, J_{HH} 7 Hz); $\delta_P(CH_2Cl_2)$ 28.0 (Found: C, 61.8; H, 9.2; N, 11.0. $C_{13}H_{23}N_2OP$ requires C, 61.4; H, 9.1; N, 11.0%).

(b) *With methylamine.* Anhydrous liquid methylamine (20—30 mol equiv.) was added to the appropriate methanesulphonate (**6**) (0.35 mmol) in a cooled sample tube. A vigorous reaction ensued and was complete within 0.5 min. Analysis as in (a) indicated only one substantial product (≥98%) which was isolated as before (some of the product was lost by extraction into the water wash). The following were obtained, following crystallisation from chloroform–ether.

N-*Methyl*-P-*methyl*-N'-*phenylphosphonic diamide* (**10**; R = Me), m.p. 160 °C, *m/z* 184 (M^+, 70%) and 93 ($Ph\overset{+\bullet}{N}H_2$, 100); $\delta_P(CH_2Cl_2)$ 25.0 (Found: C, 52.2; H, 7.1; N, 15.4. $C_8H_{13}N_2OP$ requires C, 52.2; H, 7.1; N, 15.2%).

P-*Ethyl*-N-*methyl*-N'-*phenylphosphonic diamide* (**10**; R = Et), m.p. 137.5—138.5 °C, *m/z* 198 (M^+, 60%) and 93 (100); $\delta_P(CH_2Cl_2)$ 29.9 (Found: C, 54.8; H, 7.6; N, 14.2. $C_9H_{15}N_2OP$ requires C, 54.5; H, 7.6; N, 14.1%).

P-*Isopropyl*-N-*methyl*-N'-*phenylphosphonic diamide* (**10**; R = Pr^i), m.p. 156—157 °C, *m/z* 212 (M^+, 70%) and 93 (100); $\delta_P(CH_2Cl_2)$ 32.5 (Found: C, 56.3; H, 8.0; N, 13.0. $C_{10}H_{17}N_2OP$ requires C, 56.6; H, 8.1; N, 13.2%).

The ^1H n.m.r. spectra ($CDCl_3$) of these *N*-methyl compounds were similar to those of the corresponding *N*-t-butyl compounds isolated in (a), except that the signal at δ 1.3 (9 H, s) was replaced by δ 2.55—2.60 (3 H, d, J_{PH} 12 Hz) (broadened or further split by coupling to NH), and for (**10**; R = Pr^i) the diastereotopic Me groups showed less pronounced non-equivalence (Δδ 0.03).

The diamide (**10**; R = Me) was also formed when the *O*-arylsulphonyl-*N*-(methylphenylphosphinyl)hydroxylamines (**26**; Z = *p*-tolyl or mesityl) were treated with methylamine.

(c) *With sodium methoxide in methanol.* The appropriate methanesulphonate (**6**) (0.2 mmol) suspended in methanol (0.8 ml) at room temperature was treated with sodium methoxide (0.2 ml of 2M solution). There was an immediate exothermic reaction and a solid ($NaOSO_2Me$) was precipitated. After 20 min the mixture was neutralised by addition of solid ammonium chloride (0.4 mmol), methanol was evaporated, water was added, and the product was extracted ($CDCl_3$) and examined by ^1H n.m.r. spectroscopy and by g.l.c. (3% OV 17, 190 °C). Crystallisation then afforded the following methyl *N*-phenyl-*P*-alkylphosphonamidates: (**16**; R = Me), crystallised from benzene, m.p. 76—77 °C; (**16**; R = Et), crystallised from light petroleum, m.p. 68.5—70 °C; (**16**; R = Pr^i), crystallised from light petroleum, m.p. 114.5—116 °C. Their i.r, ^1H n.m.r., and mass spectra were as previously described.[6] In each case the g.l.c. analysis showed one dominant product (≥90%) and a small amount of the methyl alkylphenylphosphinate[18] (**18**; R = Me) (10%) (also visible in the ^1H n.m.r. spectrum of the crude reaction product), (**18**; R = Et) (1.3%), or (**18**; R = Pr^i) (0.3%), but none of the alkylphenylphosphinic amide (**20**)[19] (0.5% would have been detected). Using authentic samples from previous work,[6] the methyl *N*-alkyl-*P*-phenylphosphonamidates (**17**) were shown to be absent (≤0.2% would have been detected by g.l.c. with R = Et or Pr^i, ≤1% by ^1H n.m.r. with R = Me).

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