Preparation and Characterisation of *N*-(Diphenylphosphinoyl)hydroxylamine, and Conversion into *O*-Sulphonyl Derivatives that undergo Lossen-like Rearrangement [1]

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Having previously shown that diphenylphosphinic chloride (1a) forms *O*-(diphenylphosphinoyl)-hydroxylamine (3a) with hydroxylamine, we have now established that *N*-(diphenylphosphinoyl)-hydroxylamine (2a) can be obtained in good yield by reaction of (1a) with *O*-trimethylsilylhydroxylamine followed by methanolytic removal of the silyl blocking group. The di-*p*-tolyl (2b) and bis-*p*-methoxyphenyl (2c) analogues can be prepared in a similar way. *N*-(Diphenylphosphinoyl)hydroxylamine is acetylated at the O atom with acetic anhydride, and is sulphonylated at O with methanesulphonyl chloride and toluene-*p*-sulphonyl chloride. The *N*-(diphenylphosphinoyl)-*O*-sulphonylhydroxylamines (8) and (12a) undergo rapid and quantitative Lossen-like rearrangement with methanol–sodium methoxide to give methyl *N,P*-diphenylphosphonamidate (11). Comparable rearrangements are observed with t-butylamine, aniline–triethylamine, and phenol–triethylamine.

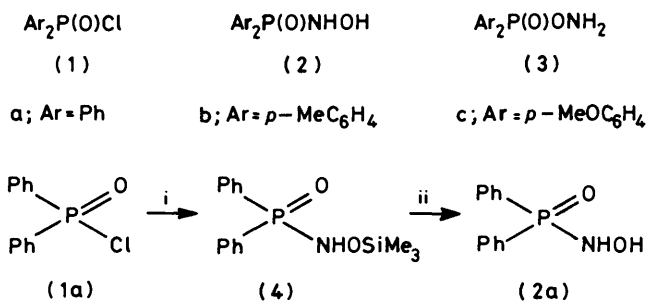
Hydroxylamine can, in principle, react with a phosphorylating agent by way of the oxygen or the nitrogen atom. In 1960 Kreutzkamp and Schindler [2] isolated a phosphinoylhydroxylamine from the reaction of diphenylphosphinic chloride (1a) with free hydroxylamine in suspension in benzene, and assigned to it the *N*-(diphenylphosphinoyl)hydroxylamine structure (2a). Since neither chemical nor spectroscopic evidence of structure was presented it seems likely that their assignment was based largely on analogy with the behaviour of acylating [3] and sulphonylating [4] agents; the isolated products in these cases are generally the *N*-substituted hydroxylamines (hydroxamic acids). We have recently re-examined the reaction of diphenylphosphinic chloride with hydroxylamine in benzene and found that the product is actually the *O*-(diphenylphosphinoyl)hydroxylamine (3a),[5] a potentially useful electrophilic aminating agent.[5,6] That being so, the question arises as to whether it is possible to prepare *N*-phosphinoylhydroxylamines such as (2a).

Results and Discussion

Considerable evidence suggests that the kinetically preferred attack of hydroxylamine on an acylating agent involves the oxygen atom,[7–9] even though the product that is isolated is almost always the (more stable) *N*-acylhydroxylamine.[3] We therefore examined first the possibility that *O*-(diphenylphosphinoyl)hydroxylamine (3a) might isomerise to the *N*-phosphinoyl compound (2a) in a solution containing free hydroxylamine. However, using ^{31}P n.m.r. spectroscopy it was seen that hydroxylamine merely increased the rate of decomposition of (3a) in methanol without causing any detectable isomerisation to (2a).

We next considered the possibility of phosphinoylating a hydroxylamine derivative in which attack by the oxygen atom was blocked. In view of the notable ease with which P–N bonds are cleaved by acid,[10] it was felt necessary to avoid blocking groups that would require even mildly acidic conditions for their removal. The trimethylsilyl group was therefore chosen, and was introduced by treatment of hydroxylamine with trimethylsilyl chloride or (more satisfactorily) hexamethyldisilazane by known procedures.[11,12]

Diphenylphosphinic chloride (1a) reacted during several hours with *O*-trimethylsilylhydroxylamine in dilute diethyl ether solution containing triethylamine (Scheme 1). After filtration to remove triethylamine hydrochloride, methanol

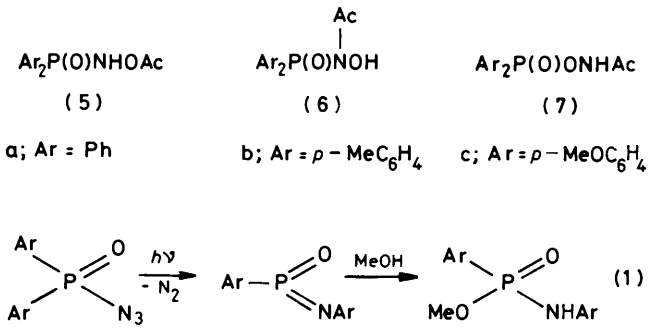


Scheme 1. *Reagents:* i, $H_2NOSiMe_3$, Et_3N; ii, MeOH

(*ca.* 3 equiv.) † was added to remove the blocking group without attempting to isolate the *N*-phosphinoyl-*O*-trimethylsilylhydroxylamine (4). The colourless solid that precipitated was clearly a (diphenylphosphinoyl)hydroxylamine (M^+ 233; elemental analysis) (34% yield) and differed from the *O*-substituted compound (3a) in a number of significant ways,[5] *e.g.* it did not react with acetone or dimethyl sulphide, nor did it immediately liberate iodine from potassium iodide, and its ^{31}P n.m.r. signal (in MeOH) appeared at a substantially higher field (δ_P 29.5 as opposed to 38.0 p.p.m.). By implication this compound must be the *N*-phosphinoylhydroxylamine (2a).

An improved method of preparation was devised, taking advantage of the extremely low solubility of *N*-(diphenylphosphinoyl)hydroxylamine (2a) in dichloromethane, and the relatively high solubility of triethylamine hydrochloride. By carrying out the reaction in dichloromethane at a suitable dilution (*ca.* 3.5 ml CH_2Cl_2 per mmol phosphinic chloride) triethylamine hydrochloride does not begin to precipitate until practically all the phosphinic chloride has reacted with *O*-trimethylsilylhydroxylamine; its appearance can thus serve as an indication of the progress of the reaction. Addition of methanol (3—4 equiv.) † produces a clear solution (dispensing with the need for filtration) from which pure *N*-(diphenylphosphinoyl)hydroxylamine slowly precipitates in good yield (≥75%). The same method is also successful for the *N*-(di-*p*-tolylphosphinoyl) (2b) and *N*-(bis-*p*-methoxyphenylphos-

† Triethylamine (0.5—1.0 equiv.) was added with the methanol to minimise the risk of acid-catalysed P–N bond cleavage, but this is probably not necessary.



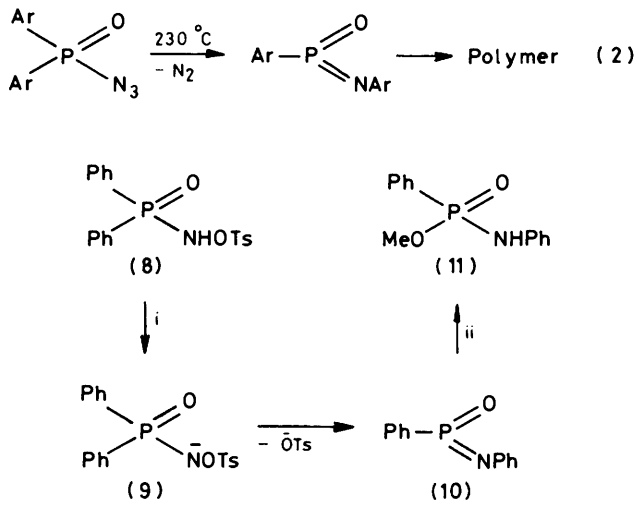
phinoyl) (2c) hydroxylamines. In these cases the initial yields are lower (*ca.* 55%) because of the less complete precipitation of the product from the reaction mixture. However, by evaporation of the filtrate and treatment of the residue with water to dissolve out triethylamine hydrochloride, useful additional quantities of product (10% and 25% respectively) can be obtained.

The i.r. spectra of the *N*-phosphinoylhydroxylamines (2) (as Nujol mulls or KBr discs) show absorption in the region 3 300—3 150 cm^{-1} (two partially resolved maxima at *ca.* 3 240 and 3 175 cm^{-1}) similar to (but broader than) that of the *O*-phosphinoyl compounds (3). In addition they contain some rather weak absorptions at *ca.* 2 900—2 850 cm^{-1} (visible only in KBr), and the P=O peaks (1 165 cm^{-1}) appear *ca.* 55 cm^{-1} lower than those of the *O*-phosphinoylhydroxylamines.[5]

The ^1H n.m.r. spectra (90 or 100 MHz) of the *N*-(diarylphosphinoyl)hydroxylamines (2) in [$^2H_6$]dimethyl sulphoxide contain signals at δ 8.3—8.0, which integrate for two protons, in addition to the aryl-group resonances. These signals appear as three slightly broadened lines (possibly with fine structure), one having twice the intensity of the others, and collapse to broadened singlets (at 60 MHz) on irradiation of the phosphorus nucleus. It seems that the NHOH group gives rise to two overlapping doublets with couplings of *ca.* 12 and 6 Hz between the protons and phosphorus.

Confirmation of the *N*-phosphinoyl structures (2) was sought by acetylation, the reactions proceeding readily with acetic anhydride–triethylamine in dichloromethane at room temperature. Although the products gave mass spectra in which the molecular ions were not of significant abundance (but $M^+ - CH_2{=}C{=}O$ peaks were prominent) their ^1H n.m.r. spectra ($CDCl_3$) included singlets at δ 8.3 (1 H, exchanged with D_2O) and 2.05 (3 H) and they analysed for monoacetates. The n.m.r. signals are consistent with the presence of the NHOAc group in structure (5) but do not necessarily rule out the alternative *N*-acetyl structures (6) and (7). However, the *O*-acetyl structure (5) is supported by the rather high i.r. carbonyl stretching frequency at 1 755 cm^{-1} (in CH_2Cl_2). Comparison with published values for related systems is not wholly convincing, *e.g.* the *O*-acyl and *N*-acyl groups of PhCONHOAc absorb at 1 765 and 1 710 cm^{-1} respectively (in $CHCl_3$)[7] whereas the corresponding groups of MeCONHOAc absorb at 1 795 and 1 725 cm^{-1} (in dioxane),[13] but comparison with the much lower carbonyl frequency (1 705 cm^{-1} in $CHCl_3$) of the monoacetates derived from the *O*-phosphinoylhydroxylamines (3),[5] and believed to have the structure (7), does seem conclusive.

A particular incentive for preparing *N*-phosphinoylhydroxylamines (phosphinohydroxamic acids) was the prospect that suitably activated derivatives would undergo Lossen-like rearrangement.[3,14] It is now well established that phosphinic azides undergo Curtius-like rearrangement on photolysis, and the intermediate monomeric metaphosphonimidates have been trapped with methanol and other nucleophiles [equation (1)].[15,16] There is also evidence for rearrangement in the non-photochemical decomposition of phosphinic azides, but this occurs only at high temperatures (>200 °C) and thermally generated monomeric metaphosphonimidates have not been trapped [equation (2)].[17] Indeed the chance of trapping with nucleophiles seems rather remote since the azides are susceptible to nucleophilic attack at phosphorus at temperatures much below those needed for thermal decomposition.[15] Our hope was that *N*-phosphinoylhydroxylamines would provide a mild non-photochemical route to monomeric metaphosphonimidates, thereby enabling a more thorough investigation of the reactions of these interesting analogues of monomeric metaphosphate.[18]

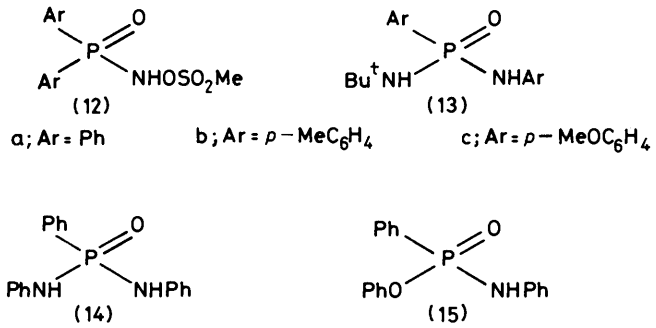


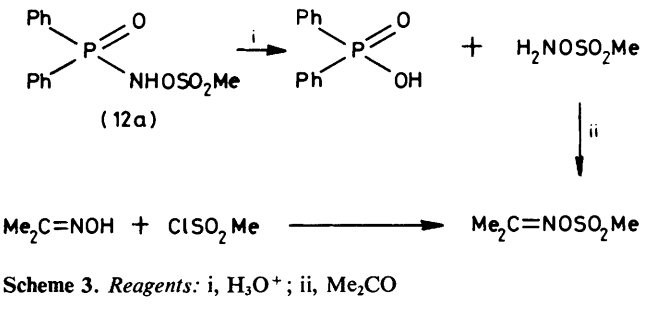
Scheme 2. *Reagents:* i, ^-OMe; ii, MeOH

Treatment of *N*-(diphenylphosphinoyl)hydroxylamine (2a) with toluene-*p*-sulphonyl chloride in pyridine afforded a monotosylate in modest yield (42%). By analogy with acetylation we have assigned the structure (8) to this product, although the spectroscopic data do not preclude the possibility of the tosyl group being attached to nitrogen. The ^{31}P n.m.r. signal in methanol appears at δ_P 29.7 p.p.m. but on addition of sodium methoxide (slight excess) this was immediately replaced by a signal at δ_P 20.2 p.p.m. Neutralisation of the solution with ammonium chloride caused no change in the spectrum, showing that the new signal was not due merely to the conjugate base (9) of the substrate (Scheme 2). The product was isolated and characterised as methyl *N*,*P*-diphenylphosphonamidate (11) (96% isolated, 100% by ^{31}P n.m.r.); it was identical with the material previously obtained [along with smaller amounts of $Ph_2P(O)OMe$, $Ph_2P(O)NH_2$, and $Ph_2P(O)NHOMe$] in the photolysis of diphenylphosphinic azide in methanol.[15b]

Clearly the Lossen-like rearrangement of the tosyl derivative of *N*-(diphenylphosphinoyl)hydroxylamine will occur rapidly and quantitatively under mild conditions. However, the preparative value of this system is somewhat diminished by the rather poor yield (42%) of the tosylation reaction. We therefore attempted to prepare the methanesulphonate of *N*-(diphenylphosphinoyl)hydroxylamine. Using methanesulphonyl chloride in pyridine the derivative (12a) was obtained in 79% yield,* and the related *N*-phosphinoylhydroxylamines (2b) and (2c) were likewise converted into the methanesulphonates (12b) and (12c) in good yield (>75%).* All the

* These are yields before recrystallisation, but the crude material appeared to be essentially pure and could be used satisfactorily in preparative reactions.





Scheme 3. *Reagents:* i, H_3O^+; ii, Me_2CO

methanesulphonates (12) are stable crystalline compounds and were obtained analytically pure without difficulty. Their ^1H n.m.r. spectra in [$^2H_6$]dimethyl sulphoxide show a distinctive low-field doublet (δ 10.6—10.9, J_{PH} 10—11 Hz), which collapses to a singlet on irradiation at phosphorus, for the NH proton. In the case of (12a) the structure was confirmed by cleavage of the P–N bond with perchloric acid (Scheme 3). This gave diphenylphosphinic acid and a compound (not characterised because of its anticipated instability) that on treatment with acetone was converted into *O*-(methylsulphonyl)acetoxime, identical with an authentic specimen (Scheme 3). The isolated yield of the oxime was only *ca.* 20%, but its formation shows that *O*-(methylsulphonyl)-hydroxylamine must have been produced in the initial cleavage reaction.

The methanesulphonate (12a) of *N*-(diphenylphosphinoyl)-hydroxylamine behaved just like the tosylate (8) with methanol–sodium methoxide, giving methyl *N*,*P*-diphenylphosphonamidate (11) in quantitative yield. Even with the comparatively weak base t-butylamine it was rapidly transformed into the rearrangement product (13a) (94% isolated yield), whose structure was confirmed by comparison with an authentic sample prepared by sequential reaction of $PhP(O)Cl_2$ with t-butylamine and aniline. The related methanesulphonates (12b) and (12c) reacted similarly with t-butylamine to give the phosphonic diamides (13b) and (13c). With the still weaker base aniline the methanesulphonate (12a) did not rearrange at room temperature (although it slowly decomposed to unidentified products) but on addition of triethylamine (2 equiv.) it was rapidly converted into the phosphonic dianilide (14) (90% isolated; 100% by ^{31}P n.m.r.). Similarly with phenol–triethylamine it gave the phenyl phosphonamidate (15).

At present we have no direct evidence concerning the mechanism of the Lossen-like rearrangements of *O*-sulphonyl-*N*-phosphinoylhydroxylamines. If, as seems likely, they proceed *via* monomeric metaphosphonimidates such as (10), the cleanness of the reactions, the mildness of the reaction conditions, and the possibility of using a wide range of trapping agents should make them ideal reactions for studying the chemistry of these reactive species. Regardless of mechanism, the rearrangements provide a convenient direct route to unsymmetrical phosphonic acid derivatives $ArP(O)(X)NHAr$ free of contamination by $ArP(O)X_2$ or $ArP(O)(NHAr)_2$.

Experimental

M.p.s were determined with a Kofler hot-stage apparatus. I.r. spectra were recorded with Perkin-Elmer 237 and 257 instruments, and ^1H n.m.r. spectra with Varian EM390 and JEOL JNM-PS-100 spectrometers except that ^{31}P-decoupled spectra were obtained using a Varian T-60 instrument coupled to an NMR Specialities HD 60 heteronuclear decoupler. ^{31}P N.m.r. spectra (^1H-decoupled) were recorded at 24.3 MHz with a JEOL JNM-FX60 spectrometer; positive chemical shifts are downfield from external 85% H_3PO_4. Mass spectra were obtained with a V.G. Micromass 16B instrument.

O-Trimethylsilylhydroxylamine.—Essentially in accordance with the procedure of Duboudin *et al.*,[12] dried and finely powdered hydroxylamine hydrochloride (17.4 g, 0.25 mol) was added to a stirred (powerful magnet) mixture of 1,1,1,3,3,3-hexamethyldisilazane (25.2 ml, 0.12 mol) and tripropylamine (49.5 ml, 0.26 mol). The flask was stoppered and the contents were stirred vigorously at room temperature for 24 h. The mixture was filtered with suction under dry nitrogen and the solid (Pr_3NHCl) was washed with a small volume of t-butylbenzene (or other inert high-b.p. solvent). The filtrate and washings were distilled in a Spaltrohr apparatus to give a small fore-run followed by *O*-trimethylsilylhydroxylamine (72%), b.p. 58—59 °C at 158 mmHg (lit.,[12] 60 °C at 160 mmHg); $\nu_{max.}$ (film) 3 320, 3 250, 3 160w, and 1 590 cm^{-1} (NH_2). The product sometimes contained a small amount of an impurity, $\nu_{max.}$ 1 050 cm^{-1} (possibly $Me_3SiOSiMe_3$), and this tended to increase on storage. However, it did not interfere with the reactions with phosphinic chlorides and even substantially contaminated material could be used provided the quantities were adjusted to allow for the presence of the impurity. (The silylated hydroxylamine was also made using trimethylsilyl chloride.[11])

Diarylphosphinic Acids and Chlorides.—Diphenyl, di-*p*-tolyl, and bis-*p*-methoxyphenylphosphinic acids and the corresponding phosphinic chlorides were prepared as previously described.[5]

N-(Diarylphosphinoyl)hydroxylamines.—(*a*) A solution of diphenylphosphinic chloride (2.00 g, 8.47 mmol) in dichloromethane (7 ml) was added during 0.3 h to a stirred solution of *O*-trimethylsilylhydroxylamine (11.4 mmol) and triethylamine (1.01 g, 10.0 mmol) in dichloromethane (25 ml) under nitrogen at room temperature. The mixture was stirred for a further 1.3 h, during which time a very small amount of solid (Et_3NHCl) separated. Methanol (0.80 g, 25 mmol) and triethylamine (0.65 g, 6.4 mmol) * were added to give a clear solution. Crystallisation of the desilylated product was initiated by scratching after *ca.* 15 min and continued for *ca.* 3 h. The product was collected by filtration and dried at 0.1 mmHg to give *N-(diphenylphosphinoyl)hydroxylamine* (2a) (1.52 g, 77%), m.p. 145—146 °C (decomp.); *m/z* 233 (M^+, 19%), 217, 216, 201 (M^+ – NHOH, 100), 199, 140, 124, and 77; $\nu_{max.}$ (Nujol) 3 250 and 3 180 (NHOH), 1 165 (P=O), 1 125, and 1 100 cm^{-1}; $\nu_{max.}$ (KBr) 3 250, 3 180, and 2 880

* Triethylamine was added with the methanol to minimise the risk of acid-catalysed P–N bond cleavage, but this is probably not necessary.

cm^{-1} (NHOH); δ_H (CD_3SOCD_3) 8.31 (2 H, m, NHOH) and 8.0—7.35 (10 H, m); δ_P (CH_3SOCH_3) 24.6 p.p.m.; δ_P (MeOH) 29.5 p.p.m. Recrystallisation from methanol did not change the m.p. or spectra (Found: C, 62.0; H, 5.2; N, 6.1. $C_{12}H_{12}NO_2P$ requires C, 61.8; H, 5.2; N, 6.0%). Other samples of this compound had m.p.s ranging from 141 to 152 °C (decomp.). In contrast to *O*-(diphenylphosphinoyl)hydroxylamine [5] it did not immediately liberate iodine from potassium iodide in acetic acid and was completely unchanged (^{31}P n.m.r. and i.r. spectroscopy) after being suspended in acetone or in dichloromethane containing dimethyl sulphide for 19 h.

(*b*) *N*-(Diphenylphosphinoyl)hydroxylamine was initially prepared (less satisfactorily) using diethyl ether as solvent, a reaction time of 17 h, and filtering off Et_3NHCl before the addition of the methanol–triethylamine; the yield was 34%.

(*c*) Using the method in (*a*) above but with a reaction time of 16 h (although reaction was probably complete in 2 h), di-*p*-tolyphosphinic chloride gave N-(*di*-p-*tolylphosphinoyl*)-*hydroxylamine* (2b) (54%), m.p. 143—144 °C (decomp.); *m/z* 261 (M^+, 15%), 245 (100), 244, 229 (M^+ − NHOH, 100), 227, 154, 138, and 91; $\nu_{max.}$ (Nujol) 3 230 and 3 170 (NHOH), 1 165 (P=O), 1 120, and 1 100 cm^{-1}; $\nu_{max.}$ (KBr) 3 230, 3 160, and 2 860 cm^{-1} (NHOH); δ_H (CD_3SOCD_3) 8.2 (2 H, m, NHOH), 7.70 (4 H, dd, J_{PH} 11, J_{HH} 8 Hz), 7.38 (4 H, dd, J_{PH} 2, J_{HH} 8 Hz), and 2.33 (6 H, s). The filtrate from the isolation of the product was freed of volatile material at 0.2 mmHg and was treated with water (15 ml). The resulting solid was filtered off, washed with water, dried, and crystallised from benzene–methanol (4 : 1) to give additional *N*-(di-*p*-tolylphosphinoyl)hydroxylamine (10%), m.p. 140—141 °C (decomp.) (Found: C, 64.8; H, 6.0; N, 5.2. $C_{14}H_{16}NO_2P$ requires C, 64.4; H, 6.2; N, 5.4%).

(*d*) Using the method in (*a*) above but with a reaction time of 16 h (although reaction appeared to be complete in 1 h), bis-*p*-methoxyphenylphosphinic chloride gave N-(*bis*-p-*methoxyphenylphosphinoyl*)*hydroxylamine* (2c) (55%), m.p. 138—140 °C (decomp.); *m/z* 293 (M^+, 9%), 277, 276, 261 (M^+ − NHOH, 100), 259, 170, 154, 123, 108, and 107; $\nu_{max.}$ (Nujol) 3 240 and 3 180 (NHOH), 1 165 (P=O), and 1 130 cm^{-1}; $\nu_{max.}$ (KBr) 3 240, 3 180, and 2 880br cm^{-1} (NHOH); δ_H (CD_3SOCD_3) 8.0 (2 H, m, NHOH), 7.63 (4 H, dd, J_{PH} 11, J_{HH} 9 Hz), 6.98 (4 H, dd, J_{PH} 3, J_{HH} 9 Hz), and 3.76 (6 H, s). Evaporation of the filtrate and treatment with water as in (*c*) gave an additional crop of the product (25%) which was crystallised from dichloromethane–methanol at −20 °C, m.p. 139—140 °C (decomp.) (Found: C, 57.2; H, 5.6; N, 4.9. $C_{14}N_{16}NO_4P$ requires C, 57.3; H, 5.5; N, 4.8%).

O-*Acetyl*-N-(*diarylphosphinoyl*)*hydroxylamines*.—In a typical preparation *N*-(diphenylphosphinoyl)hydroxylamine (2a) (0.117 g, 0.50 mmol) was suspended in dichloromethane (2.5 ml) and the mixture was stirred while triethylamine (0.076 g, 0.75 mmol) and then acetic anhydride (0.077 g, 0.75 mmol) were added. After 15 min a clear solution was obtained. After 40 min the mixture was diluted with dichloromethane (3 ml), washed with water (3 × 2 ml), and dried (Na_2SO_4). The residue remaining after evaporation of the solvent was purified by dissolution in a very small volume of dichloromethane and dilution with diethyl ether; crystals of O-*acetyl*-N-(*diphenylphosphinoyl*)*hydroxylamine* (5a) (0.114 g, 83%) were obtained, m.p. 164—165 °C; *m/z* 233 (M^+ − CH_2=C=O, 60%) (no M^+ 275 observed); $\nu_{max.}$ (Nujol) 3 100 (NH), 1 785 (C=O), 1 215, and 1 190 cm^{-1} (P=O); $\nu_{max.}$ (CH_2Cl_2) 1 755 cm^{-1} (C=O); δ_H ($CDCl_3$) 8.32 (1 H, s, exchanged with D_2O), 8.0—7.7 (4 H, m), 7.55—7.25 (6 H, m), and 2.04 (3 H, s) (Found: C, 61.2; H, 5.2; N, 5.1. $C_{14}H_{14}NO_3P$ requires C, 61.1; H, 5.1; N, 5.1%).

The following were similarly prepared: O-*acetyl*-N-(*di*-p-*tolylphosphinoyl*)*hydroxylamine* (5b), m.p. 127—129 °C (from CH_2Cl_2–diethyl ether); *m/z* 303 (M^+, 0.5%) and 261 (M^+ − CH_2=C=O, 40); $\nu_{max.}$ (Nujol) 3 020 (NH), 1 775 (C=O), and 1 190 cm^{-1} (P=O); $\nu_{max.}$ (CH_2Cl_2) 1 755 cm^{-1} (C=O); δ_H ($CDCl_3$) 8.25 (1 H, s, exchanged with D_2O), 7.77 (4 H, dd, J_{PH} 12, J_{HH} 8 Hz), 7.22 (4 H, dd, J_{PH} 3, J_{HH} 8 Hz), 2.36 (6 H, s), and 2.05 (3 H, s) (Found: C, 63.3; H, 6.1; N, 4.65. $C_{16}H_{18}NO_3P$ requires C, 63.4; H, 6.0; N, 4.6%); and O-*acetyl*-N-(*bis*-p-*methoxyphenylphosphinoyl*)*hydroxylamine* (5c), m.p. 121.5—122.5 °C; *m/z* 335 (M^+, 2%) and 293 (M^+ − CH_2=C=O, 40); $\nu_{max.}$ (Nujol) 3 020 (NH), 1 765 (C=O), and 1 210 cm^{-1} (P=O); $\nu_{max.}$ (CH_2Cl_2) 1 755 cm^{-1} (C=O); δ_H ($CDCl_3$) 8.25 (1 H, s), 7.83 (4 H, dd, J_{PH} 11, J_{HH} 9 Hz), 7.00 (4 H, dd, J_{PH} 3, J_{HH} 9 Hz), 3.84 (6 H, s), and 2.05 (3 H, s) (Found: C, 57.7; H, 5.4; N, 4.3. $C_{16}H_{18}NO_5P$ requires C, 57.3; H, 5.4; N, 4.2%).

N-(*Diphenylphosphinoyl*)-O-(p-*tolylsulphonyl*)*hydroxylamine* (8).—A suspension of *N*-(diphenylphosphinoyl)hydroxylamine (0.583 g, 2.5 mmol) in pyridine (4 ml) was stirred and cooled in ice and recrystallised toluene-*p*-sulphonyl chloride (0.525 g, 2.75 mmol) was added. After the mixture had been stirred at room temperature for 0.5 h a further portion of toluene-*p*-sulphonyl chloride (0.143 g, 0.75 mmol) was added. A clear solution was eventually obtained. After a total of 1.8 h the solution was poured into ice–water (30 ml). The resulting sticky mass was stirred for 0.5 h to give a fine solid which was filtered off and dried over P_2O_5 at 0.1 mmHg. The crude product (0.447 g) was purified by dissolution in warm chloroform (1.5 ml), filtration of the solution, and addition of diethyl ether (6 ml) to precipitate N-(*diphenylphosphinoyl*)-O-(p-*tolylsulphonyl*)*hydroxylamine* (8) (0.405 g, 42%) which was recrystallised from methanol–water (1 : 1) (brief heating), m.p. 133—134 °C (decomp.); *m/z* 387 (M^+, 3%), 217 (70), 216 (100), and 199 (80); $\nu_{max.}$ (Nujol) 3 020 (NH), 1 380, and 1 205 cm^{-1}; δ_H ($CDCl_3$) 8.15 (1 H, s, NH), 7.8—7.1 (14 H, m), and 2.42 (3 H, s); δ_P (CH_2Cl_2) 28.6 p.p.m. (Found: C, 59.1; H, 4.7; N, 3.5. $C_{19}H_{18}NO_4PS$ requires C, 58.9; H, 4.7; N, 3.6%).

N-(*Diarylphosphinoyl*)-O-*methylsulphonylhydroxylamines*.—Typically, *N*-(diphenylphosphinoyl)hydroxylamine (0.466 g, 2.00 mmol) and pyridine (1.5 ml) were mixed thoroughly to give a paste, methanesulphonyl chloride (0.276 g, 2.40 mmol) was added, and the mixture was shaken for 8 min or until a clear solution resulted. The solution was immediately poured, with efficient mixing, into ice–water (15 ml). After *ca.* 10 min the precipitate was filtered off, washed with water, and dried over P_2O_5 at 0.2 mmHg to give N-(*diphenylphosphinoyl*)-O-*methylsulphonylhydroxylamine* (12a) (0.492 g, 79%), m.p. 149 °C (decomp.); after crystallisation from methanol, m.p. 149 °C (decomp.); *m/z* 311 (M^+, 18%); $\nu_{max.}$ (Nujol) 3 140 (NH), 1 370, 1 200, and 1 180 cm^{-1}; δ_H (CD_3SOCD_3) 10.91 (1 H, d, J_{PH} 11 Hz), 8.0—7.3 (10 H, m), and 3.26 (3 H, s); δ_P (CH_3SOCH_3) 27.2 p.p.m.; δ_P (MeOH) 30.7 p.p.m. (Found: C, 50,1; H, 4.5; N, 4.5; P, 10.25. $C_{13}H_{14}NO_4PS$ requires C, 50.2; H, 4.3; N, 4.5; P, 9.95%).

The following were prepared in the same way: N-(*di*-p-*tolylphosphinoyl*)-O-*methylsulphonylhydroxylamine* (12b) (81%), m.p. 154.5 °C (decomp.) after crystallisation from methanol; *m/z* 339 (M^+, 13%); $\nu_{max.}$ (Nujol) 3 140 (NH), 1 370, 1 195, and 1 175 cm^{-1}; δ_H (CD_3SOCD_3) 10.77 (1 H, d, J_{PH} 10 Hz), 7.69 (4 H, dd, J_{PH} 12, J_{HH} 9 Hz), 7.38 (4 H, dd, J_{PH} 3, J_{HH} 9 Hz), 3.25 (3 H, s), and 2.37 (6 H, s) (Found: C, 53.2; H, 5.3; N, 4.2; P, 8.8. $C_{15}H_{18}NO_4PS$ requires C, 53.1; H, 5.35; N, 4.1; P, 9.1%); and N-(*bis*-p-*methoxyphenylphosphinoyl*)-O-*methylsulphonylhydroxylamine* (12c) (77%), m.p. 140—141 °C (decomp.) after crystallisation from methanol; $\nu_{max.}$ (Nujol) 3 080 (NH), 1 370, 1 200, 1 185, and 1 175 cm^{-1}; δ_H (CD_3SOCD_3) 10.60 (1 H, d, J_{PH} 10 Hz), 7.69 (4 H, dd, J_{PH} 12, J_{HH} 9

Hz), 7.08 (4 H, dd, J_{PH} 3, J_{HH} 9 Hz), 3.80 (6 H, s), and 3.23 (3 H, s) (Found: C, 48.5; H, 4.9; N, 3.7. $C_{15}H_{18}NO_6PS$ requires C, 48.5; H, 4.9; N, 3.8%).

These methanesulphonates were stored at −45 °C although when pure they appear to be stable for months at room temperature. When their i.r. spectra were recorded in KBr additional (weak) absorptions at *ca.* 2 800 cm^{-1} became apparent.

To confirm the structure, *N*-(diphenylphosphinoyl)-*O*-methylsulphonylhydroxylamine (73 mg) was degraded by being stirred with 60% perchloric acid (0.5 ml) for 10 min. This gave an insoluble oily solid, which on crystallisation from aqueous ethanol afforded diphenylphosphinic acid (30 mg, 58%), and a solution that was diluted by addition to ice–water (3 ml) and then was extracted with dichloromethane (4 ml, then 2 × 2 ml). The extracts were briefly dried (Na_2SO_4) and acetone (3 ml) was added. After 0.5 h volatile material was evaporated to leave a residue (12.2 mg) which had an n.m.r. spectrum consistent with a mixture (*ca.* 3 : 1) of *O*-methylsulphonylacetoxime and diphenylphosphinic acid. The residue was extracted with hot diethyl ether–light petroleum (b.p. 40—60 °C) (2 : 1) and the extract was cooled to 0 °C to give *O*-methylsulphonylacetoxime, m.p. 43—45 °C, i.r. and mass spectra as for an authentic sample prepared as follows. A mixture of acetoxime (110 mg, 1.5 mmol) and methanesulphonyl chloride (172 mg, 1.5 mmol) in dichloromethane 1.0 ml) was maintained at room temperature for 0.8 h. The solution was then washed with water, dried (Na_2SO_4), and evaporated under reduced pressure, and the residue was crystallised from diethyl ether–light petroleum (b.p. 40—60 °C) at 0 °C to give O-*methylsulphonylacetoxime* (84 mg, 37%), m.p. 45—46 °C; *m/z* 151 (M^+, 8%), 79 (16), and 72 (100); $\nu_{max.}$ (melt) 1 360, 1 180, 970, 880, 840, and 790 cm^{-1}; δ_H ($CDCl_3$) 3.13 (3 H, s) and 2.03 (6 H, s) (Found: C, 32.0; H, 6.0; N, 9.2. $C_4H_9NO_3S$ requires C, 31.8; H, 6.0; N, 9.3%).

Reactions of N-(*Diarylphosphinoyl*)-O-*sulphonylhydroxylamines.*—(a) *With methanol–sodium methoxide. N*-(Diphenylphosphinoyl)-*O*-(*p*-tolylsulphonyl)hydroxylamine (63.7 mg, 0.165 mmol) was dissolved in slightly warm methanol (1.2 ml) and the ^{31}P n.m.r. spectrum was recorded. Sodium methoxide (0.20 mmol) was added and the spectrum run again, showing that the original peak at δ_P 29.7 p.p.m. had been completely replaced by one at δ_P 20.2 p.p.m. Quenching with ammonium chloride (0.1 mmol) did not cause any change in the spectrum. Methanol was evaporated off and the residue was partitioned between dichloromethane (8 ml) and water (2 ml). The organic layer was separated, washed with water, dried (Na_2SO_4), and evaporated to dryness. The residue was crystallised by being dissolved in a few drops of dichloromethane and the solution diluted with light petroleum (b.p. 60—80 °C) to give methyl *N,P*-diphenylphosphonamidate (11) (39.1 mg, 96%), m.p. 122—123 °C (lit.,[19] 123.5—125 °C); *m/z* 247 (M^+, 100%), 155 (M^+ − NHPh, 45), and 77 (50); $\nu_{max.}$ (Nujol) 3 160 (NH), 1 210 (P=O), and 1 040 cm^{-1} (POMe); δ_H ($CDCl_3$) 7.95—7.25 (5 H, m, PPh), 7.25—6.7 (6 H, m, NPh and NH), and 3.78 (3 H, d, J_{PH} 11 Hz) [in dilute solution the NH signal appeared at δ 6.4 (1 H, br d, J_{PH} 6 Hz)]; δ_P (CH_2Cl_2) 18.6 p.p.m.

A similar experiment was carried out using *N*-(diphenylphosphinoyl)-*O*-methylsulphonylhydroxylamine (δ_P 30.7 p.p.m. in MeOH). The quenched (NH_4Cl) reaction mixture was examined by g.l.c. (3% OV 17 at 250 °C) which showed the presence of a single product (R_t 9.5 min) and confirmed (with authentic samples) the absence of $Ph_2P(O)OMe$ (R_t 5.4 min), $Ph_2P(O)NHOMe$ (R_t 11.9 min), and $Ph_2P(O)NH_2$ (R_t 12.2 min). Methyl *N,P*-diphenylphosphonamidate was isolated and characterised as above, in quantitative yield.

(b) *With t-butylamine. N*-(Diphenylphosphinoyl)-*O*-methylsulphonyl)hydroxylamine (68.4 mg, 0.22 mmol) was added to t-butylamine (0.3 ml); a slightly exothermic reaction ensued. After 0.5 h the excess of amine was evaporated off and the residue was dissolved in dichloromethane (5 ml). The solution was washed with water and dried (Na_2SO_4). Evaporation of the solvent and trituration of the residue with diethyl ether afforded N′,P-*diphenyl*-N-*t-butylphosphonic diamide* (13a) (59.6 mg, 94%), crystallised from benzene, m.p. 176—178 °C; *m/z* 288 (M^+, 100%); $\nu_{max.}$ (Nujol) 3 380 and 3 250 cm^{-1} (NH); δ_H ($CDCl_3$) 8.0—7.3 (5 H, m, PPh), 7.2—6.75 (5 H, m, NPh), 5.24 (1 H, br d, J_{PH} 9 Hz), 2.79 (1 H, br d, J_{PH} 11 Hz), and 1.32 (9 H, s) (Found: C, 66.9; H, 7.3; N, 9.6. $C_{16}H_{21}N_2OP$ requires C, 66.65; H, 7.3; N, 9.7%). The structure was confirmed by comparison with an authentic sample prepared by the reaction of phenylphosphonic dichloride with t-butylamine (2 equiv.) in diethyl ether to give *P*-phenyl-*N*-t-butylphosphonamidic chloride (crystallised from diethyl ether, m.p. 96—99 °C) which was then treated with aniline in the presence of pyridine.

Similarly, *N*-(di-*p*-tolylphosphinoyl)-*O*-methylsulphonylhydroxylamine gave N′,P-*di*-p-*tolyl*-N-*t-butylphosphonic diamide* (13b) (91%), crystallised from benzene–light petroleum, m.p. 197—198 °C; *m/z* 316 (M^+, 87%); $\nu_{max.}$ (Nujol) 3 260 cm^{-1} (NH); δ_H ($CDCl_3$) 7.69 (2 H, dd, J_{PH} 13, J_{HH} 8 Hz), 7.14 (2 H, dd, J_{PH} 3, J_{HH} 8 Hz), 6.90 (4 H, s, NAr), 5.26 (1 H, br d, J_{PH} 7 Hz), 2.81 (1 H, br s), 2.33 (3 H, s), 2.20 (3 H, s), and 1.30 (9 H, s) (Found: C, 68.5; H, 8.0; N, 9.0. $C_{18}H_{25}N_2OP$ requires C, 68.3; H, 8.0; N, 8.9%), and *N*-(bis-*p*-methoxyphenylphosphinoyl)-*O*-methylsulphonylhydroxylamine gave N′,P-*bis*-p-*methoxyphenyl*-N-*t-butylphosphonic diamide* (13c) (100%), crystallised from benzene, m.p. 151—153 °C (softens at lower temperature); *m/z* 348 (M^+, 52%); $\nu_{max.}$ (Nujol) 3 160 cm^{-1} (NH); δ_H ($CDCl_3$) 7.72 (2 H, dd, J_{PH} 12, J_{HH} 9 Hz), 6.87 (2 H, dd, J_{PH} 3, J_{HH} 9 Hz), 6.80 (centre of 4 H, AA′BB′ pattern), 5.11 (1 H, br d, J_{PH} 8 Hz), 3.78 (3 H, s), 3.69 (3 H, s), 2.76 (1 H, br s), and 1.31 (9 H, s) (Found: C, 62.2; H, 7.3; N, 8.1. $C_{18}H]_{25}N_2O_3P$ requires C, 62.05; H, 7.2; N, 8.0%).

(c) *With aniline–triethylamine. N*-(Diphenylphosphinoyl)-*O*-methylsulphonylhydroxylamine (62.2 mg, 0.20 mmol) was suspended in aniline (0.3 ml). Addition of triethylamine (40.4 mg, 0.40 mmol) caused an immediate exothermic reaction and formation of a clear solution. After 0.5 h the mixture was diluted with methanol and examined by ^{31}P n.m.r. spectroscopy; a single peak (δ_P 11.7 p.p.m.) was observed. Volatile material was removed under reduced pressure and water (3 ml) was added, together with just sufficient HCl to make the water acidic. The resulting solid was filtered off, washed thoroughly with water, and dried to give *N,N′,P*-triphenylphosphonic diamide (14) (55.0 mg, 90%), *m/z* 308 (M^+, 100%); $\nu_{max.}$ (Nujol) 3 120 (NH) (identical with the i.r. spectrum of an authentic sample prepared from phenylphosphonic dichloride and aniline), crystallised from ethanol, m.p. 213—214 °C (lit.,[20] 211—212 °C).

For a similar reaction with no triethylamine, ^{31}P n.m.r. spectroscopy (in MeOH) showed that even after 17 h the methanesulphonate (δ_P 30.8 p.p.m.) was largely (70—80%) unchanged and that no *N,N′,P*-triphenylphosphonic diamide had been formed. The products [δ_P 26.0 and 25.0 p.p.m. (trace)] were not characterised. The unchanged methanesulphonate was isolated (33%) and its identity was confirmed by i.r. spectroscopy.

(d) *With phenol–triethylamine.* To a suspension of *N*-(diphenylphosphinoyl)-*O*-methylsulphonylhydroxylamine (62.2 mg, 0.20 mmol) in dichloromethane (0.5 ml) was added phenol (75.2 mg, 0.80 mmol) and then triethylamine (40.4 mg 0.40 mmol). After 1 h a clear solution was obtained, δ_P 15.1 p.p.m. (one peak only). Volatile material was removed under reduced pressure and the resulting oil was triturated with water (containing a little Et_3N) until a non-sticky solid was

obtained. Filtration and drying afforded phenyl *N,P*-diphenylphosphonamidate (15) (52.0 mg, 84%), crystallised from aqueous ethanol, m.p. 146—147 °C (lit.,[21] 145—146 °C); *m/z* 309 (M^+, 100%); $\nu_{max.}$ (Nujol) 3 180 (NH), 1 225, 1 195, 950, and 920 cm^{-1}; δ_P (CH_2Cl_2) 14.3 p.p.m.; δ_H ($CDCl_3$) 8.0—7.3 (5 H, m, PPh), 7.3—6.7 (10 H, m, NPh and OPh), and 6.35 (1 H, br d, J_{PH} 6 Hz). [The characteristics of this compound depended markedly on the method of isolation, *e.g.* crystallisation from benzene–light petroleum gave material having a different i.r. spectrum (Nujol) and a m.p. *ca.* 20 °C lower.]

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