O-(Diphenylphosphinyl)hydroxylamine: Preparation and Some Characteristic Chemical Reactions [1]

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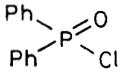
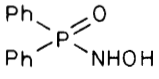
Hydroxylamine reacts with diphenylphosphinic chloride (1) in benzene (or aqueous dioxan) to give *O*-(diphenylphosphinyl)hydroxylamine (3) and not the *N*-phosphinyl compound (2) as was previously thought. Di-*p*-tolyl-, bis-*p*-methoxyphenyl-, and phenyl-*p*-methoxyphenyl-phosphinic chlorides are similarly attacked by the oxygen of hydroxylamine. The structures of the phosphinylhydroxylamines can be inferred from their chemical reactions; in particular they condense with acetone to give phosphinylacetone oximes (8) identical to those obtained from phosphinic chlorides and acetone oxime. Like *O*-sulphonylhydroxylamines, *O*-(diphenylphosphinyl)hydroxylamine forms aminophosphonium and aminosulphonium salts with triphenylphosphine and dimethyl sulphide respectively.

HYDROXYLAMINE, a nucleophile displaying the α-effect,[2] reacts rapidly with acylating agents.[3] Both the oxygen and nitrogen atoms can act as nucleophiles, but attack by oxygen seems to be kinetically preferred.[4-6] The resulting *O*-acylhydroxylamines have occasionally been isolated under carefully controlled conditions,[4] but usually it is the *N*-acylhydroxylamine (hydroxamic acid) that is the isolated product.[7] With sulphonyl halides hydroxylamine likewise gives *N*-sulphonyl derivatives under preparative conditions.[8]

The high nucleophilicity of hydroxylamine towards phosphorus centres [2,3,9] has influenced the search for compounds able to reactivate phosphorylated acetylcholinesterase,[10] and has led to antidotes containing *N*-hydroxy-groups.[11] Kinetic studies suggest that it is the oxygen atom in hydroxylamine that initially attacks a phosphorylating agent [12] but there are apparently no reports of *O*-phosphorylhydroxylamines having been isolated. In 1960 Kreutzkamp and Schindler [13] isolated the product from the reaction of free hydroxylamine with diphenylphosphinic chloride (1) in benzene. This had m.p. 131 °C (decomp.) and analysed for $C_{12}H_{12}NO_2P$. It was designated *N*-(diphenylphosphinyl)hydroxylamine (2) although no chemical or spectroscopic evidence of structure was presented. In particular, the *O*-phosphinyl structure (3) was apparently not considered.



(1)



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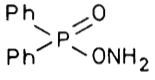


(3)

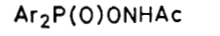
For this reason a more thorough examination of the reactions of phosphinic chlorides with hydroxylamine seemed called for.

RESULTS AND DISCUSSION

As in the reported procedure,[13] a suspension of free hydroxylamine (2.2 equiv.) in benzene was treated with diphenylphosphinic chloride (1) (0.35 h at *ca.* 5 °C then 0.5 h at 5—15 °C). The precipitate was collected, washed with iced water (to remove hydroxylamine hydrochloride), and crystallised from methanol. The resulting compound gradually decomposed when heated above 130 °C, had *m/e* 233 (M^+), and analysed for $C_{12}H_{12}NO_2P$ (92% yield before crystallisation). Presumably this phosphinylhydroxylamine is the same as that previously isolated by Kreutzkamp and Schindler.[13] Similar experiments with di-*p*-tolyl, bis-*p*-methoxyphenyl, and phenyl-*p*-methoxyphenylphosphinic chlorides likewise gave phosphinylhydroxylamines (60—89% yield before crystallisation).

The mass spectra and ^{31}P n.m.r. chemical shifts are not helpful in determining whether the phosphinyl groups are attached to oxygen or nitrogen. The ^1H n.m.r. spectra (in $CDCl_3$) include broad singlets at *ca.* δ 5.7 caused by two exchangeable protons.† These signals are entirely reasonable for the NH_2 groups in structures such as (3) but are not necessarily incompatible with the presence of NHOH groups as in (2). The situation is similar for the i.r. spectra (as Nujol mulls) which contain absorptions at *ca.* 3 270 (usually >1 peak) and 3 170 (NH and/or OH) and at *ca.* 1 210 cm^{-1} (P=O). Although the rather high P=O frequency is more obviously compatible with an *O*-phosphinyl structure such as (3) ‡ it does not conclusively rule out the *N*-phosphinyl alternative. Attempts were therefore made to establish the structures by chemical means.

The phosphinylhydroxylamines react readily with acetic anhydride in dichloromethane at 25 °C. The crystalline derivatives are monoacetates and have i.r. absorptions (in $CHCl_3$) at *ca.* 3 120 (NH) and 1 705 cm^{-1} (C=O). The two most reasonable structures are (4) and (5), and of these it is the *N*-acetyl (*O*-phosphinyl) form (4) that accords better with the position of the carbonyl



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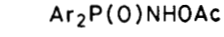

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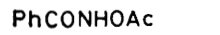


(6)

(7)

† The diphenylphosphinyl compound is practically insoluble in chloroform and other unreactive aprotic solvents; n.m.r. data relate only to the other, more soluble, phosphinylhydroxylamines.

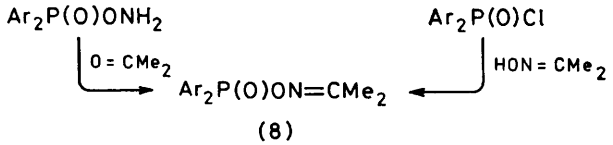
‡ Ref. 14 quotes P=O frequencies of 1220—1181 cm^{-1} for $R_2P(O)OR$ and 1180—1156 cm^{-1} for $R_2P(O)NHR$.

absorption. In particular the *O*-acetyl group of (5) would be expected to show a substantially higher carbonyl frequency. Thus, for example, the *O*-acyl and *N*-acyl groups of (6) absorb at 1 765 and 1 710 cm^{-1} respectively (in $CHCl_3$),[4] and the corresponding groups of (7) absorb at 1 795 and 1 725 cm^{-1} (in dioxan).[15]

O-Acylhydroxylamines are known to act as oxidants, liberating iodine from potassium iodide.[16] Our phosphinylhydroxylamines behave similarly; when added to potassium iodide in acetic acid, iodine and the corresponding phosphinic acid are formed immediately. The amount of iodine liberated is consistent with the reaction shown in equation (1).

$$Ph_2P(O)ONH_2 + 2I^- + 3H^+ \longrightarrow Ph_2P(O)OH + I_2 + NH_4^+ \quad (1)$$

Our phosphinylhydroxylamines condense with acetone at room temperature. The ^1H n.m.r. spectra of the products indicate the presence of two non-equivalent methyl groups (typically δ 2.06 and 1.91) as would be the case for the *O*-phosphinylacetone oximes (8). Since



(8)

SCHEME

these same products can be obtained by treating acetone oxime with diarylphosphinic chlorides (Scheme) their structures seem secure. That being so, the hydroxylamines must surely be the *O*-phosphinyl compounds [*e.g.* (3)] and not the *N*-phosphinyl compounds [*e.g.* (2)] originally suggested by Kreutzkamp and Schindler.[13]

Mechanistic studies with phosphorylating agents in aqueous solution have afforded indirect evidence for initial attack by the oxygen atom of hydroxylamine.[12] Proof, however, requires that the phosphorylhydroxylamines be isolated from aqueous media and characterised. We find that addition of diphenylphosphinic chloride (1) in dioxan to a cold, concentrated aqueous solution of hydroxylamine (generated *in situ* from hydroxylamine hydrochloride and sodium hydroxide) results in the rapid precipitation of a colourless solid. This is identical to the product obtained using free hydroxylamine in benzene, and is therefore *O*-(diphenylphosphinyl)hydroxylamine (3).* We have not examined phosphorylating (as distinct from phosphinylating) agents but our results may encourage attempts to isolate *O*-phosphorylhydroxylamines.

O-Sulphonylhydroxylamines must in general be prepared by indirect methods, rather than directly from hydroxylamine,† and they are mostly rather unstable.[17,18] Nonetheless, their ability to aminate phosphines,[19] sulphides,[20] and other nucleophiles [17] makes them important synthetic reagents. The possibility of the more readily accessible *O*-phosphinylhydroxylamines exhibiting similar reactivity is obviously worth considering. In fact we find that *O*-(diphenylphosphinyl)hydroxylamine in dichloromethane reacts rapidly and quantitatively with triphenylphosphine [equation (2)] and dimethyl sulphide [equation (3)] to give the amino-

$$Ph_3P + H_2NOP(O)Ph_2 \longrightarrow Ph_3\overset{+}{P}NH_2\ \bar{O}P(O)Ph_2 \quad (2)$$

$$Me_2S + H_2NOP(O)Ph_2 \longrightarrow Me_2\overset{+}{S}NH_2\ \bar{O}P(O)Ph_2 \quad (3)$$

phosphonium and aminosulphonium salts. However, it does not react readily (if at all) with pyridine (in CH_2Cl_2) or sodium phthalimide (in aqueous MeOH or dimethylformamide), in contrast to *O*-mesitylsulphonyl-[21] and *O*-(2,4-dinitrophenyl)-hydroxylamine [22] respectively. Thus the relatively poor leaving ability of phosphinate seems likely to limit the synthetic applications of *O*-phosphinylhydroxylamines.

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 T-60 and EM390 spectrometers, tetramethylsilane as internal standard. ^{31}P N.m.r. spectra 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.

Free, crystalline, hydroxylamine was prepared from the hydrochloride by the method of Hurd; [23] it could be stored for several weeks in sealed vessels at −40 °C and was always handled in an atmosphere of dry nitrogen. Acetoxime was obtained as described by Vogel.[24]

Diarylphosphinic Acids.—Diphenylphosphinic acid and di-*p*-tolylphosphinic acid were as previously described.[25] Bis-*p*-methoxyphenylphosphinic acid, m.p. 179—181 °C (lit.,[26] 180—181 °C), was prepared by the general procedure of Kosolapoff and Struck [27] using diethyl phosphite and *p*-methoxyphenylmagnesium bromide followed by bromine oxidation, δ($CDCl_3$) 10.5 (1 H, s), 7.54 (4 H, dd, J_{PH} 12, J_{HH} 9 Hz), 6.76 (4 H, dd, J_{PH} 3, J_{HH} 9 Hz), and 3.76 (6 H, s). Phenyl-*p*-methoxyphenylphosphinic acid was obtained by hydrolysis of the product of the reaction of dichlorophenylphosphine with *p*-methoxybenzenediazonium tetrafluoroborate (Cu_2Cl_2 catalyst); the procedure of Mann *et al.*[28] was followed except that heat was applied to initiate reaction (bath *ca.* 75 °C) and the acid was isolated simply by diluting the final reaction mixture to *ca.* 35% water (by volume) and setting aside to slowly crystallise. After recrystallisation from ethanol the acid (65%) had m.p. 182—183 °C (lit.,[28] 184 or 183.5—185.5 °C), δ($CDCl_3$) 9.40 (1 H, s), 7.9—7.2 (7 H, m), 6.85 (2 H, dd, J_{PH} 3, J_{HH} 8 Hz), and 3.79 (3 H, s).

Diarylphosphinic Chlorides.—Diphenylphosphinic chlor-

* This method of preparation is extremely simple and has the particular advantage that it avoids the tiresome preparation of free hydroxylamine. Yields so far have not been high (64%) but no attempt has yet been made to optimise the procedure.

† *O*-Sulphonylhydroxylamines can, however, be obtained by direct sulphonylation using the *N*-protected hydroxylamine derivative $LiON(SiMe_3)_2$ followed by hydrolytic removal of the *N*-trimethylsilyl groups [F. D. King and D. R. M. Walton, *Synthesis*, 1975, 788].

ide and di-*p*-tolylphosphinic chloride were as previously described.[25] Bis-*p*-methoxyphenylphosphinic chloride, b.p. 205—210 °C (oven temp.) at 0.3 mmHg (lit.,[26] 216 °C at 0.05 mmHg), and phenyl-*p*-methoxyphenylphosphinic chloride, b.p. 190 °C (oven temp.) at 0.6 mmHg (solidifies when cool), $\nu_{max.}$ (melt) 1 600, 1 505, 1 260, 1 235, and 1 120 cm^{-1}, $\delta(CDCl_3)$ 8.1—7.4 (7 H, m), 7.05 (2 H, dd, J_{PH} 4, J_{HH} 9 Hz), and 3.90 (3 H, s), were prepared by heating the appropriate phosphinic acid with an excess of thionyl chloride (*ca.* 4 ml per g of acid) for 1.5—2.0 h and distilling the product under vacuum.

Preparation of O-(*Diarylphosphinyl*)*hydroxylamines.* (*a*) A suspension of hydroxylamine (0.28 g, 8.4 mmol) in dry benzene (7 ml) was stirred vigorously at *ca.* 5 °C under nitrogen. Diphenylphosphinic chloride (0.91 g, 3.85 mmol) in benzene (5 ml) was added dropwise over 0.3 h, during which time much solid separated. Stirring was continued for a further 0.5 h as the mixture was allowed to warm gradually to room temperature. The solid was collected by filtration, sucked free of benzene, washed thoroughly with several portions of ice-cold water (a little sodium hydroxide being added to the first portion to assist removal of any phosphinic acid present in the solid), and dried over phosphorus pentaoxide at room temperature and 0.1 mmHg. The crude phosphinylhydroxylamine (0.82 g, 3.53 mmol, 92%) was 94% pure by iodometry (see below). Crystallisation from methanol, with only brief heating, afforded pure O-(*diphenylphosphinyl*)*hydroxylamine*, m.p. >130 °C (gradual decomp.), *m/e* 233 (M^+, 17%), 217 (4%), and 201 ($M^+ - ONH_2$, 48%), $\nu_{max.}$ (Nujol) 3 280, 3 270, and 3 180 (NH), 1 640, 1 615, 1 595, 1 210 (P=O), and 900 cm^{-1} (Found: C, 61.7; H, 5.2; N, 6.2; P, 13.4. $C_{12}H_{12}NO_2P$ requires C, 61.8; H, 5.2; N, 6.0; P, 13.3%). This compound was only sparingly soluble in most aprotic organic solvents (ether, $CHCl_3$, CH_2Cl_2, *etc.*) and suffered decomposition in some (acetone, dimethyl sulphoxide).

(*b*) Aqueous hydroxylamine hydrochloride (6.6M; 1.65 mmol) was treated with aqueous sodium hydroxide (7.1M; 1.4 mmol) and dioxan (0.8 ml) added. The mixture was cooled in ice and stirred vigorously while diphenylphosphinic chloride (0.6 mmol) in dioxan (0.6 ml) was added in a single portion. The mixture was shaken for 3—4 min, diluted with water, and filtered to give crude *O*-(diphenylphosphinyl)hydroxylamine (64%) which was purified and characterised as in (*a*) above. Acidification of the filtrate gave some diphenylphosphinic acid.

(*c*) Di-*p*-tolylphosphinic chloride was added to hydroxylamine in benzene and the crude product (73%) was isolated as described in (*a*) above. Evaporation of the benzene filtrate afforded a little di-*p*-tolylphosphinic acid (11%). The crude product was dissolved in dichloromethane (30 ml g^{-1}) and the solution shaken with iced water to which sufficient sodium hydroxide was added to make it just alkaline. The solution was then washed with water, dried (Na_2SO_4), and concentrated under reduced pressure at room temperature. Addition of ether gave O-(*di*-p-*tolylphosphinyl*)*hydroxylamine*, m.p. 112 °C (decomp.), *m/e* 261 (M^+, 15%), 233 (30%), and 229 ($M^+ - ONH_2$, 75%), $\nu_{max.}$ (Nujol) 3 280br and 3 170 (NH), 1 605, 1 220, 1 200 (P=O), and 885 cm^{-1}, $\delta(CDCl_3)$ 7.68 (4 H, dd, J_{PH} 12, J_{HH} 8 Hz), 7.22 (4 H, dd, J_{PH} 4, J_{HH} 8 Hz), 5.82 br (2 H, s) (exchanged with D_2O), and 2.36 (6 H, s), δ_P ($CDCl_3$) 36.9 (Found: C, 64.5; H, 6.15; N, 5.7; P, 11.5. $C_{14}H_{16}NO_2P$ requires C, 64.4; H, 6.2; N, 5.4; P, 11.9%).

(*d*) Bis-*p*-methoxyphenylphosphinic chloride was converted into *O*-(bis-*p*-methoxyphenylphosphinyl)hydroxylamine (89% crude) as in (*c*) above. Crystallisation from chloroform–ether gave a product, m.p. 87—88 °C which was still contaminated with chloroform (n.m.r. spectroscopy and elemental analysis) after pumping for 2 h at 0.3 mmHg. Crystallisation at −20 °C from ether containing a little methanol afforded O-(*bis*-p-*methoxyphenylphosphinyl*)*hydroxylamine*, m.p. 92.5—93.5 °C (decomp.), $\nu_{max.}$ (Nujol) 3 280, 3 270, and 3 170 (NH), 1 605, 1 210 (P=O), and 890 cm^{-1}, $\delta(CDCl_3)$ 7.70 (4 H, dd, J_{PH} 12, J_{HH} 8 Hz), 6.91 (4 H, dd, J_{PH} 3, J_{HH} 8 Hz), 5.85br (2 H, s), and 3.80 (6 H, s), δ_P ($CDCl_3$) 38.3 (Found: C, 57.9; H, 5.6; N, 4.9; P, 10.2. $C_{14}H_{16}NO_4P$ requires C, 57.35; H, 5.5; N, 4.8; P, 10.55%).

(*e*) Phenyl-*p*-methoxyphenylphosphinic chloride and hydroxylamine gave, by the method in (*c*) above, O-(*phenyl*-p-*methoxyphenylphosphinyl*)*hydroxylamine* (60% crude), m.p. 78.5—79.5 °C (from dichloromethane–ether at −20 °C), *m/e* 263 (M^+, 6%) and 231 ($M^+ - ONH_2$, 23%), $\nu_{max.}$ (Nujol) 3 310, 3 270, 3 230, and 3 170 (NH), 1 605, 1 205 (P=O), and 890 cm^{-1}, $\delta(CDCl_3)$ 8.0—7.2 (7 H, m), 6.92 (2 H, dd, J_{PH} 3, J_{HH} 9 Hz), 5.62br (2 H, s) (exchanged with D_2O), and 3.81 (3 H, s) (Found: C, 59.6; H, 5.4; N, 5.4; P, 11.3. $C_{13}H_{14}NO_3P$ requires C, 59.3; H, 5.4; N, 5.3; P, 11.8%).

The *O*-(diarylphosphinyl)hydroxylamines could be stored at −40 °C for several months but gradually decomposed (especially in solution) at room temperature. The crystallisation procedures described above sometimes resulted in considerable loss of material. For most purposes the crude products were satisfactory.

Reaction of O-(*Diarylphosphinyl*)*hydroxylamines with Potassium Iodide.*—All of the *O*-(diarylphosphinyl)hydroxylamines immediately liberated iodine from potassium iodide in acetic acid or aqueous methanol. In two cases the reaction was investigated more closely. Thus crude *O*-(diphenylphosphinyl)hydroxylamine (0.030 g) in glacial acetic acid (1.2 ml) was treated with 3.6M-aqueous potassium iodide solution (0.2 ml). Iodine was instantly formed. After 0.5 h the mixture was diluted with water and titrated against 0.050M-sodium thiosulphate solution, indicating the yield of iodine to be 0.94 mol/mol of the crude hydroxylamine. Using recrystallised material the yield was 1.00 mol/mol. When the end-point was reached the mixture was made strongly acidic (HCl); diphenylphosphinic acid (90%), m.p. 190—192 °C, crystallised out. Using *O*-(di-*p*-tolylphosphinyl)hydroxylamine the yields of iodine were 0.88 (crude) and 0.97 (recrystallised) mol/mol, and di-*p*-tolylphosphinic acid (93%), m.p. 136.5—137.5 °C, was isolated.

N-*Acetyl*-O-(*diarylphosphinyl*)*hydroxylamines.*— In a typical preparation, crude *O*-(di-*p*-tolylphosphinyl)hydroxylamine (0.090 g, 0.34 mmol) was suspended in dichloromethane (0.8 ml) and acetic anhydride (0.15 ml) was added. The mixture was kept at 25 °C for 0.5 h with occasional shaking. Volatile matter was removed under vacuum and the residue dissolved in dichloromethane. The solution was washed with water, dried (Na_2SO_4), and concentrated. The solid obtained on addition of ether was recrystallised from dichloromethane–ether to give, after drying for 2 h at 50 °C and 0.3 mmHg, N-*acetyl*-O-(*di*-p-*tolylphosphinyl*)-*hydroxylamine* (0.067 g, 0.22 mmol, 65%), m.p. 140—141.5 °C, *m/e* 303 (M^+, 9%), 261 ($M^+ - CH_2{=}C{=}O$, 14%), 248, 247, 246, 245, and 229 ($M^+ - ONHAc$, 100%), $\nu_{max.}$ (Nujol) 3 090 (NH), 1 725 (C=O), 1 600m, 1 215, 1 200 (P=O), and 840 cm^{-1}, $\nu_{max.}$ ($CHCl_3$) 3 120 and 1 705 cm^{-1},

δ($CDCl_3$) 11.8br (1 H, s), 7.77 (4 H, dd, J_{PH} 12, J_{HH} 8 Hz), 7.21 (4 H, dd, J_{PH} 3, J_{HH} 8 Hz), 2.36 (6 H, s), and 1.89 (3 H, s) (Found: C, 63.4; H, 6.0; N, 4.8. $C_{16}H_{18}NO_3P$ requires C, 63.4; H, 6.0; N, 4.6%).

The following were similarly prepared: N-*acetyl*-O-(*diphenylphosphinyl*)*hydroxylamine* (64%), m.p. 131—133 °C (from dichloromethane–ether), *m/e* 275 (M^+, 11%), 233 (M^+ — CH_2CO, 35%), 218 (35), 217 (50), and 201 (M^+ — ONHAc, 100), $\nu_{max.}$ (Nujol) 3 110 (NH), 1 725 (C=O), 1 595w, 1 220 (P=O), and 835 cm^{-1}, $\nu_{max.}$ ($CHCl_3$) 3 120 and 1 705 cm^{-1}, δ($CDCl_3$) 11.8br (1 H, s), 8.1—7.2 (10 H, m), and 1.90 (3 H, s) (Found: C, 61.15; H, 5.1; N, 5.2. $C_{14}H_{14}NO_3P$ requires C, 61.1; H, 5.1; N, 5.1%); N-*acetyl*-O-(*bis*-p-*methoxyphenylphosphinyl*)*hydroxylamine*, m.p. 128—131 °C (from benzene–light petroleum), $\nu_{max.}$ (Nujol) 3 100 (NH), 1 720 (C=O), 1 600, 1 215 (P=O), and 830 cm^{-1}, $\nu_{max.}$ ($CHCl_3$) 3 110 and 1 705 cm^{-1}, δ($CDCl_3$) 12.0br (1 H, s), 7.83 (4 H, dd, J_{PH} 12, J_{HH} 8 Hz), 6.90 (4 H, dd, J_{PH} 3, J_{HH} 8 Hz), 3.80 (6 H, s), and 1.89 (3 H, s) (Found: C, 57.5; H, 5.4; N, 4.2. $C_{16}H_{18}NO_5P$ requires C, 57.3; H, 5.4; N, 4.2%); and N-*acetyl*-O-(*phenyl*-p-*methoxyphenylphosphinyl*)*hydroxylamine* (80%), m.p. 132—133 °C from dichloromethane–ether, *m/e* 305 (M^+, 10%), 263 (M^+ — CH_2CO, 15%), 250, 249, 248, 247, and 231 (M^+ — ONHAc, 100%), $\nu_{max.}$ (Nujol) 3 120 (NH), 1 715 (C=O), 1 595, 1 210 (P=O), and 825 cm^{-1}, $\nu_{max.}$ ($CHCl_3$) 3 120 and 1 705 cm^{-1}, δ($CDCl_3$) 11.8br (1 H, s), 8.0—7.25 (7 H, m), 6.91 (2 H, dd, J_{PH} 3, J_{HH} 9 Hz), 3.79 (3 H, s), and 1.89 (3 H, s) (Found: C, 58.2; H, 5.3; N, 4.55. $C_{15}H_{16}NO_4P$ requires C, 59.0; H, 5.3; N, 4.6%).

O-(*Diarylphosphinyl*)*acetone Oximes*.—These were prepared in two ways. (*a*) A suspension of the *O*-(diarylphosphinyl)hydroxylamine (0.40 mmol) in acetone (2.0 ml) was kept at 25 °C for 2 h and shaken occasionally. The resulting clear solution was evaporated under reduced pressure and the residue recrystallised to give the *O*-(diarylphosphinyl)acetone oxime (*ca.* 65%).

(*b*) A solution of the diarylphosphinic chloride (1.0 mmol) in dichloromethane (1.5 ml) was added to a solution of acetoxime (2.0 mmol) in the same solvent (1.5 ml). After 1 h at room temperature the mixture was diluted with more dichloromethane, washed with water, dried (Na_2SO_4), and evaporated under reduced pressure. Crystallisation of the residue afforded the *O*-(diarylphosphinyl)acetone oxime, identical (i.r., n.m.r.) to that obtained in (*a*).

The following compounds were prepared by both methods: O-(*diphenylphosphinyl*)*acetone oxime*, m.p. 117—119 °C [from dichloromethane–ether (1 : 4)], *m/e* 273 (M^+, 6%), 201 (M^+ — $ONCMe_2$, 100%), and 133 (M^+ — $PhPO_2$, 58%), $\nu_{max.}$ (Nujol) 1 225 cm^{-1} (P=O), δ($CDCl_3$) 8.0—7.25 (10 H, m), 2.06 (3 H, s), and 1.91 (3 H, s) (Found: C, 65.8; H, 6.0; N, 5.05. $C_{15}H_{16}NO_2P$ requires C, 65.9; H, 5.9; N, 5.1%); O-(*di*-p-*tolylphosphinyl*)*acetone oxime*, m.p. 77—78 °C [from ether–light petroleum (b.p. 40—60 °C)], *m/e* 301 (M^+, 11%), 229 (M^+ — $ONCMe_2$, 100%), and 147 (M^+ — $ArPO_2$, 43%), $\nu_{max.}$ (Nujol) 1 230 cm^{-1} (P=O), δ($CDCl_3$) 7.69 (4 H, dd, J_{PH} 12, J_{HH} 8 Hz), 7.20 (4 H, dd, J_{PH} 4, J_{HH} 8 Hz), 2.36 (6 H, s), 2.04 (3 H, s), and 1.90 (3 H, s) (Found: C, 67.8; H, 6.8; N, 4.7. $C_{17}H_{20}NO_2P$ requires C, 67.8; H, 6.7; N, 4.65%); O-(*bis*-p-*methoxyphenylphosphinyl*)*acetone oxime*, m.p. 78—79 °C [from ether (at low temperature)], *m/e* 333 (M^+, 19%), 261 (M^+ — $ONCMe_2$, 100%), and 163 (M^+ — $ArPO_2$, 7%), $\nu_{max.}$ (Nujol) 1 230 cm^{-1} (P=O), δ($CDCl_3$) 7.70 (4 H, dd, J_{PH} 12, J_{HH} 9 Hz), 6.90 (4 H, dd, J_{PH} 3, J_{HH} 9 Hz), 3.79 (6 H, s), 2.02 (3 H, s), and 1.91 (3 H, s) (Found: C, 61.3; H, 5.9; N, 4.25. $C_{17}H_{20}NO_4P$ requires C, 61.25; H, 6.05; N, 4.2%) (a different sample of this compound had m.p. 75—76 °C); and O-(*phenyl*-p-*methoxyphenylphosphinyl*)*acetone oxime*, m.p. 72—73 °C [from ether (at low temperature)], *m/e* 303 (M^+, 18%), 231 (M^+ — $ONCMe_2$, 100%), 163 (M^+ — $PhPO_2$, 10%), and 133 (M^+ — $ArPO_2$, 8%), $\nu_{max.}$ (Nujol) 1 230 cm^{-1} (P=O), δ($CDCl_3$) 7.9—7.2 (7 H, m), 6.91 (2 H, dd, J_{PH} 3, J_{HH} 9 Hz), 3.79 (3 H, s), 2.03 (3 H, s), and 1.90 (3 H, s) (Found: C, 63.7; H, 6.0; N, 4.7. $C_{16}H_{18}NO_3P$ requires C, 63.4; H, 6.0; N, 4.6%).

Reaction of O-(*Diphenylphosphinyl*)*hydroxylamine with Triphenylphosphine*.—A solution of triphenylphosphine (0.173 g, 0.66 mmol) in dichloromethane (0.5 ml) was added during 3 min (exothermic) to a stirred suspension of *O*-(diphenylphosphinyl)hydroxylamine (0.140 g, 0.60 mmol) in dichloromethane (1.0 ml). The clear solution obtained after a further 5 min was concentrated to one-half of its original volume and diluted with ether (3 ml) to give colourless crystals of *aminotriphenylphosphonium diphenylphosphinate* (0.294 g, 0.595 mmol, 99%), $\delta_P(CH_2Cl_2)$ 34.1 and 14.9, δ_P(MeOH) 35.1 and 19.6, $\nu_{max.}$ (KBr) 3 100—2 400, 1 440, 1 200, 1 125, 1 045, and 865br cm^{-1}, m.p. 205—207 °C [after recrystallisation from dichloromethane–ether (1 : 1)] (Found: C, 72.3; H, 5.45; N, 2.85; P, 12.5. $C_{30}H_{27}NO_2P_2$ requires C 72.7; H, 5.5; N, 2.8; P, 12.5%).

To confirm the structure, a solution of the above salt (0.124 g, 0.25 mmol) in methanol (0.4 ml) was added dropwise with stirring to a solution of ammonium hexafluorophosphate (0.270 g, 1.6 mmol) in water (0.5 ml). Much solid deposited. After 15 min water (2 ml) was added and the solid was filtered off, washed with water, and dried under vacuum over phosphorus pentaoxide to give aminotriphenylphosphonium hexafluorophosphate (0.99 g, 0.234 mmol, 96%), m.p. 181—183.5 °C, raised to 187.5—188.5 °C (lit.,[29] 185—187°) by recrystallisation from aqueous methanol, $\nu_{max.}$ (Nujol) 3 435 and 3 340 (NH_2), 1 120 (P=O), and *ca.* 850br cm^{-1}, δ_P(MeOH) 35.3 and —145.0 (septet, J_{PF} 708 Hz).

Reaction of O-(*Diphenylphosphinyl*)*hydroxylamine with Dimethyl Sulphide*.—Dimethyl sulphide (0.074 g, 1.2 mmol) in dichloromethane (0.3 ml) was added to a stirred suspension of *O*-(diphenylphosphinyl)hydroxylamine (0.129 g, 0.55 mmol) in dichloromethane (1.2 ml). After 10 min a clear solution was obtained and after 0.5 h much solid deposited. After 1 h ether (2 ml) was added and the mixture was filtered to give colourless, hygroscopic, *aminodimethylsulphonium diphenylphosphinate* (0.162 g, 0.55 mmol, 100%), m.p. 145—147 °C, $\nu_{max.}$ (KBr) 3 600—2 500br (maximum at 3 330), 1 170, 1 125, and 1 040 cm^{-1}, δ(CD_3OD) 7.85—7.15 (10 H, m) and 2.91 (6 H, s); after recrystallisation from methanol–ether (1 : 8), m.p. 148—149 °C (decomp.) (Found: C, 54.1; H, 6.35; N, 4.62. $C_{14}H_{18}NO_2PS\cdot 0.9H_2O$ requires C, 54.1; H, 6.4; N, 4.5%).

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