N-Phosphonoyl and *N*-Phosphoroyl Hydroxylamines: Reactions of their *O*-Sulphonyl Derivatives with t-Butylamine

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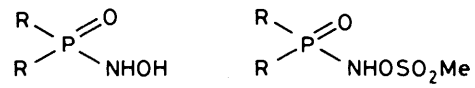
The *N*-phosphonoylhydroxylamines Ph(ArO)P(O)NHOH (Ar = *p*-chlorophenyl or *p*-tolyl) and the *N*-phosphoroylhydroxylamines $(ArO)_2P(O)NHOH$ (Ar = *p*-chlorophenyl or *p*-tolyl) have been prepared and converted into their *O*-methanesulphonyl and *O*-*p*-nitrobenzenesulphonyl derivatives. In the reactions of the sulphonyl derivatives with t-butylamine, the phosphonoyl compounds undergo a Lossen-like rearrangement with migration of the phenyl group from phosphorus to nitrogen. The phosphoroyl compounds do not rearrange with t-butylamine but give products that include $(ArO)_2P(O)NH_2$ and $(ArO)_2P(O)NHNHBu^t$.

Although a number of *N*-phosphinoylhydroxylamines have been prepared in recent years, they have all been of the type (**1**) in which the groups R are alkyl or aryl, *i.e.* they have all contained two C–P bonds.[1,2] Their *O*-sulphonyl derivatives (**2**) have proved to be of particular interest because with base they readily undergo a Lossen-like rearrangement.[1,2] In the present work our aim was to prepare analogues of (**1**) having one or both of the C–P bonds replaced by O–P bonds, and to see whether their *O*-sulphonyl derivatives would also rearrange with base. In choosing the substituents on phosphorus we were influenced by the fact that the examples of (**1**) that we have been able to isolate have all been solids, decomposing at (or below) the melting point. It therefore seemed prudent to choose groups, such as *p*-substituted phenoxy, that would be likely to give solid products.



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

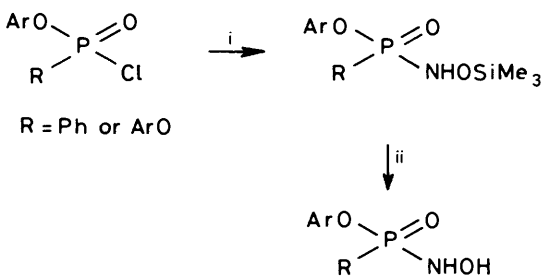
R = alkyl or aryl

Results and Discussion

Using *O*-trimethylsilylhydroxylamine the appropriate phosphorus acid chlorides were converted into the *N*-phosphonoyl and *N*-phosphoroyl hydroxylamines (**3**)—(**6**) (X = NHOH)

(**3**) Ar = *p*-ClC_6H_4 (**5**) Ar = *p*-ClC_6H_4

(**4**) Ar = *p*-MeC_6H_4 (**6**) Ar = *p*-MeC_6H_4

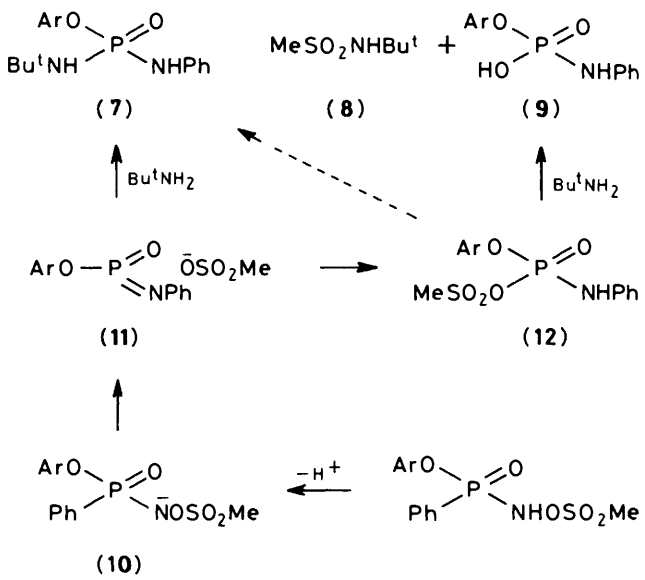


R = Ph or ArO

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

(Scheme 1). By modifying the preparative details, particularly the isolation procedure, to suit each case, the products were obtained in reasonable overall yield (>50%). They all melted with decomposition but were obtained essentially pure by careful crystallisation. An unexpected observation, given that (**1**; R = Ph) rapidly rearranges with base (NaOMe),[3] was the formation of a stable salt (or salt-like complex) when (**5**; X = NHOH) was treated with triethylamine. On reaction with methanesulphonyl chloride in pyridine for a few minutes at 0 °C the hydroxylamines all formed reasonably stable crystalline *O*-sulphonyl derivatives (X = NHOMs). These gave ^1H n.m.r. spectra containing, as expected, lowfield (δ 8.6—8.1 in $CDCl_3$) NH signals split into doublets (*J* 7—13 Hz) by coupling to phosphorus.

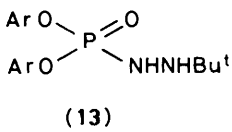
In looking for Lossen-like rearrangements of the sulphonates we used the moderately non-nucleophilic base t-butylamine, so as to reduce the risk of displacing aryloxy groups from phosphorus without unduly diminishing the efficiency of trapping of any monomeric metaphosphorimidates [*e.g.* (**11**)] that might be formed. In spite of this, substantial amounts of *p*-chlorophenol were formed in the reaction of (**3**; X = NHOMs) with t-butylamine, and although the phosphoric diamide rearrangement product (**7**; Ar = *p*-chlorophenyl) was observed its yield was only *ca.* 20%. Since (**7**) is stable in t-butylamine, it seems that the phenol must have been displaced directly from the substrate by nucleophilic attack or eliminated from its conjugate base (**10**). In the expectation that *p*-cresol (pK_a 10.2) would not be lost as readily as *p*-chlorophenol (pK_a 9.2) we turned our attention to the *p*-tolyl compound (**4**; X = NHOMs). Like the *p*-chlorophenyl compound, this reacted rather slowly with t-butylamine [over a period of hours, in contrast to the rapid exothermic reactions of the phosphinoyl compounds (**2**)], but now there was very little liberation of the phenol. The rearrangement product (**7**; Ar = *p*-tolyl) (δ_P 1.6) was isolated in 54% yield. Examination of the reaction mixture by ^{31}P n.m.r. spectroscopy revealed another substantial product (δ_P – 6.0; 27% yield). This was soluble in water, and was identified as the $Bu^tNH_3^+$ salt of the phosphoramidic acid (**9**; Ar = *p*-tolyl) by comparison with an authentic sample. The acid (**9**) is formally the product of the addition of water to the monomeric metaphosphorimidate (**11**), but we do not believe that that is how it was formed. During chromatographic isolation of the product (**7**) a compound lacking phosphorus and having the same R_F value and ^1H n.m.r. spectrum as *N*-t-butylmethanesulphonamide (**8**) was detected. Significantly its yield (25%) was about the same as that of (**9**). We suggest that following the rearrangement, the resulting metaphosphorimidate and sulphonate anion recombine to some extent to give the mixed phosphoramidic sulphonic anhydride (**12**) (Scheme 2).



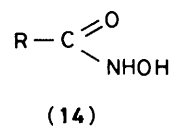
Scheme 2.

Nucleophilic attack at sulphur by t-butylamine, or base-induced formation of a sulphene ($CH_2 = SO_2$), would then give (**8**) and (**9**) in equal amount. In principle, the attack on the anhydride could occur at phosphorus instead of sulphur, and this, rather than the free metaphosphorimidate (**11**), may be responsible for at least some of the phosphoric diamide (**7**). No complications were encountered in our earlier work with the phosphinoyl compounds (**2**), the expected phosphonic diamides [RP(O)(NHBu^t)(NHR)] being the only substantial products. If mixed anhydrides were formed in those reactions, it seems they must have broken down entirely by attack at phosphorus. That is what one might predict, and what seems actually to happen in the reactions of the limited number of mixed phosphoric sulphonic anhydrides that have been reported in the literature.[4] While having no satisfactory explanation for the different behaviour of (**12**), we thought it likely that replacing methanesulphonate in the substrate by a better and less nucleophilic sulphonate leaving group would lead to a cleaner reaction. This change should both reduce the tendency of the sulphonate anion to combine with the metaphosphorimidate, and make any mixed anhydride that is still formed more liable to attack at phosphorus (with displacement of sulphonate) rather than at sulphur. The *p*-nitrobenzenesulphonate (**4**; X = NHONs) was therefore prepared by brief treatment of (**4**; X = NHOH) with *p*-nitrobenzenesulphonyl chloride in pyridine at 0 °C. Following reaction with t-butylamine the ^{31}P n.m.r. spectrum of the reaction mixture now showed only one phosphorus-containing product (δ_P 1.4) and the phosphoric diamide (**7**) was isolated in good yield (73% after purification). The fact that this reaction was much faster than that of the methanesulphonate encouraged us to look again at the *p*-chlorophenyl system (**3**). We hoped that with *p*-nitrobenzenesulphonate as the leaving group the rearrangement would be so fast that the unwanted phenol-releasing side reactions would not be able to compete. This proved to be the case, and the phosphoric diamide (**7**) was obtained in high yield (77% after purification).

In none of the foregoing rearrangements did we see evidence of migration by the aryloxy group, and it was therefore of considerable interest to see how the sulphonyl derivatives of the phosphorylhydroxylamines (**5**) and (**6**) (X = NHOH) would behave with base. The methanesulphonate (**6**; X = NHOMs) proved to be so unreactive that it could be dissolved in aqueous NaOH and recovered unchanged by acidification 10 min later. When dissolved in Bu^{t}NH$_2$–CH_2Cl_2 (1:1) it took 3 days at room temperature for reaction to reach completion. The major product (δ_P 2.2) was the phosphoric amide (**6**; X = NH_2) (66% by ^{31}P n.m.r; 42% isolated), formally derived from the triplet phosphoroylnitrene by hydrogen abstraction. Two other substantial products were detected by ^{31}P n.m.r. spectroscopy, the Bu^{t}NH$_3^+$ salt of the phosphoric acid (**6**; X = OH) (δ_P − 12.1; *ca.* 20%) and an unidentified compound (δ_P − 7.3; *ca.* 15%). The corresponding *p*-nitrobenzenesulphonate (**6**; X = NHONs) reacted more quickly (*ca.* 4 h in neat Bu^{t}NH$_2$ at 0 °C) and gave much less of the amide and the acid (≤8% each). The major product (δ_P − 0.7; 70%) was a compound not seen previously. From the ^{1}H n.m.r. spectrum it was clear that NHBu^t had been incorporated and that the $(ArO)_2PO$ group was still intact, although the outstanding feature was a second NH signal at lower field (δ 4.84) having a remarkable 35 Hz coupling to phosphorus. This suggested the phosphoroylhydrazine structure (**13**; Ar = *p*-tolyl) and the identification was confirmed by preparing identical material from $(ArO)_2P(O)Cl$ and t-butylhydrazine. The hydrazine (**13**) may be formed by insertion of the singlet nitrene into an NH bond of t-butylamine, but as it was not obtained from the methanesulphonate [which nevertheless gave a product derived (formally) from the triplet nitrene] this seems rather unlikely. More probable is that *p*-nitrobenzenesulphonate, but not methanesulphonate, is a good enough leaving group to be displaced from the substrate by nucleophilic attack of t-butylamine at nitrogen. The *p*-nitrobenzenesulphonate derivative of (**5**; X = NHOH) likewise gave the phosphoroylhydrazine (**13**; Ar = *p*-chlorophenyl) with t-butylamine, although in this case the reaction was less clean and the yield only 30%.



(**13**)



(**14**)

Although we cannot be sure that none of the minor products of the reactions described in this paper result from aryloxy migration, it is clear that this is not a major pathway and probably does not occur at all. That being so, our *N*-phosphonoyl- and *N*-phosphoroyl-hydroxylamines behave like their acyl counterparts. Thus, for example, the *N*-acylhydroxylamines (**14**; R = EtO, PhO *etc.*) form *O*-sulphonyl or *O*-phosphoroyl derivatives that do not rearrange with base but can give rise to nitrenes.[5–7]

Experimental

Instrumentation, and the preparation of *O*-trimethylsilylhydroxylamine, were as previously described.[1] Evaporation of solvents was always carried out under reduced pressure with only minimal heating.

N-[*Phenyl*(p-*chlorophenoxy*)*phosphinoyl*]*hydroxylamine* (**3**; X = NHOH).—A solution of *p*-chlorophenyl phenylphosphonochloridate[8] (1.01 g, 3.54 mmol) in dichloromethane (1 ml) was added dropwise at 0 °C to a stirred mixture of *O*-trimethylsilylhydroxylamine (0.42 g, 4.0 mmol) and triethylamine (0.36 g, 3.54 mmol) in dichloromethane (4.5 ml). Stirring was continued at room temperature for a further 1.2 h. Ether (20 ml) was added, the mixture filtered (to remove Et_3NHCl), and the filtrate evaporated. Desilylation was accomplished by adding methanol (4 ml) and after 10 min removing volatile matter (including Me_3SiOMe) under reduced pressure. The

residue was dissolved in fresh methanol (2 ml) and ice was added gradually with efficient mixing. The crude product (0.68 g, 68%) separated as an oil that solidified. It was purified by dissolution in warm dichloromethane (25 ml), concentration of the solution to *ca.* 7 ml followed by dilution with an equal volume of light petroleum (b.p. 60—80 °C), and cooling to −20 °C; this gave crystals of the *hydroxylamine* (**3**; X = NHOH) (0.57 g, 57%), m.p. 78—80 °C (decomp.), $\nu_{max.}$ (Nujol) 3 230 (NHOH) and 1 205 cm^{-1} (P = O); δ (CD_3SOCD_3) 8.34 (1 H, br d, J_{PH} 6 Hz), 8.31 (1 H, d, J_{PH} 18 Hz), 8.0—7.5 (5 H, m), and 7.45—7.15 (4 H, AA'BB' pattern centred at 7.32) (Found: C, 50.9; H, 3.9; N, 4.9; P, *ca.* 10.4. $C_{12}H_{11}ClNO_3P$ requires C, 50.8; H, 3.9; N, 4.9; P, 10.9%).

N-[*Phenyl*(p-*cresyl*)*phosphinoyl*]*hydroxylamine* (**4**; X = NHOH).—This compound was prepared from *p*-tolyl phenylphosphonochloridate[8] (7.4 g, 27 mmol) as above but with a reaction time of 2 h. Desilylation was accomplished by adding methanol (15 ml) directly to the reaction mixture (no filtration) and stirring at 0 °C for 15 min. Volatile matter was removed under reduced pressure and the oily residue was washed thoroughly with iced water and then triturated with methanol (3 ml). Water (20 ml) was added and the crude product (5.5 g, 77%) was collected by filtration. Recrystallisation from aqueous methanol afforded the pure *hydroxylamine* (**4**; X = NHOH), m.p. 96—98 °C (decomp.), $\nu_{max.}$ (Nujol) 3 240 (NHOH) and 1 205 cm^{-1} (P = O); δ (CD_3SOCD_3) 8.30 (1 H, br s), 8.21 (1 H, d, J_{PH} 17 Hz), 8.0—7.25 (5 H, m), 7.07 (4 H, s), and 2.21 (3 H, s) (Found: C, 59.7; H, 5.5; N, 5.05. $C_{13}H_{14}NO_3P$ requires C, 59.3; H, 5.4; N, 5.3%).

N-[*Bis*(p-*chlorophenoxy*)*phosphinoyl*]*hydroxylamine* (**5**; X = NHOH).—A solution of bis-*p*-chlorophenyl phosphorochloridate[9] (0.51 g, 1.5 mmol) in dichloromethane (0.4 ml) was added dropwise at 0 °C to a stirred mixture of *O*-trimethylsilylhydroxylamine (0.17 g, 1.65 mmol) and pyridine (0.12 g, 1.5 mmol) in dichloromethane (1.5 ml). After 2.5 h at room temperature the silyl blocking group was removed by adding methanol (2.5 ml) and leaving for 15 min. Volatile matter was removed under reduced pressure and the residue was partitioned between ether (10 ml) and water (8 ml). The ether layer was dried (Na_2SO_4) and evaporated. The resulting crude product was purified by dissolution in dichloromethane (2.5 ml) and gradual dilution of the solution with light petroleum (b.p. 60—80 °C); this gave crystals of the *hydroxylamine* (**5**; X = NHOH) (0.32 g, 65%), m.p. 86—87.5 °C (decomp.) (after recrystallisation), $\nu_{max.}$ 3 350, 3 170 (NHOH), and 1 190 cm^{-1} (P = O); δ (CD_3SOCD_3) *ca.* 8.7 (br, 1 H), 8.68 (1 H, d, J_{PH} 27 Hz), and 7.5—7.2 (8 H, AA'BB' pattern centred at 7.35) (addition of a *trace* of Et_3N changed the broad signal at 8.7 to a sharp d, J_{PH} 7 Hz) (Found: C, 43.05; H, 3.0; N, 4.2; P, *ca.* 8.6. $C_{12}H_{10}Cl_2NO_4P$ requires C, 43.1; H, 3.0; N, 4.2; P, 9.3%). When a solution in chloroform was treated with triethylamine (≥1 mol equiv.) and the solution concentrated and diluted with ether, a *salt* precipitated, m.p. 106—108.5 °C, $\nu_{max.}$ (Nujol) 3 260, 3 110, 1 275, and 1 215 cm^{-1}; δ ($CDCl_3$) 7.12 (8 H, s), 6.19 (2 H, br s), 3.28 (6 H, q, J_{HH} 7 Hz), and 1.19 (9 H, t, J_{HH} 7 Hz) (Found: C, 49.7; H, 5.75; N, 6.4; P, *ca.* 6.85. $C_{18}H_{25}Cl_2N_2O_4P$ requires C, 49.7; H, 5.8; N, 6.4; P, 7.1%).

N-(*Di*-p-*cresylphosphinoyl*)*hydroxylamine* (**6**; X = NHOH).—Di-*p*-tolyl phosphorochloridate[9] (8.3 g, 28 mmol) in dichloromethane (10 ml) was added at 0 °C over 10 min to a stirred mixture of *O*-trimethylsilylhydroxylamine (3.6 g, 34 mmol) and triethylamine (2.8 g, 28 mmol) in dichloromethane (30 ml). After a further 5 h at room temperature, volatile matter was evaporated, ether (60 ml) was added, and the solid (Et_3NHCl) was filtered off. The filtrate was treated with methanol (3 ml) for 10 min to effect desilylation and was then evaporated to dryness. The resulting solid was washed with ether to afford the *hydroxylamine* (**6**; X = NHOH) (4.3 g, 53%), which was recrystallised from benzene, m.p. 93—95 °C (decomp), *m/z* 293 (M^+, 12%); $\nu_{max.}$ (Nujol) 3 245 (NHOH) and 1 200 cm^{-1} (P = O); δ ($CDCl_3$) 7.05 (8 H, s), 5.53 (br, 2 H), and 2.24 (6 H, s) (Found: C, 57.6; H, 5.5; N, 4.8. $C_{14}H_{16}NO_4P$ requires C, 57.3; H, 5.5; N, 4.8%).

O-*Sulphonyl Derivatives of* N-*Phosphonoyl and* N-*Phosphoroyl Hydroxylamines.*—While being cooled at 0 °C the hydroxylamine was mixed well with anhydrous pyridine (1—2 ml g^{-1}) and methanesulphonyl chloride (*ca.* 1.5 mol equiv.) or *p*-nitrobenzenesulphonyl chloride (1.2 mol equiv.) was added. The mixture was shaken for *ca.* 10 min at 0 °C and then added with agitation to iced water (*ca.* 20 × volume of pyridine). Usually a solid precipitated, or an oil that soon solidified. If an oil persisted, the water was decanted off and the oil was triturated with methanol until a solid formed; fresh water was then added. The product was collected, dried *in vacuo*, and recrystallised (brief heating only). The following were prepared.

O-*Methylsulphonyl*-N-[*phenyl*(p-*chlorophenoxy*)*phosphinoyl*]*hydroxylamine* (**3**; X = NHOMs). This compound (81% crude) was crystallised from chloroform–ether, m.p. 154 °C (change in appearance at 125 °C), $\nu_{max.}$ (Nujol) 3 040 (NH) and 1 190 cm^{-1} (P = O); δ ($CDCl_3$) 8.63 (1 H, d, J_{PH} 7 Hz), 8.1—7.35 (5 H, m), 7.22 (4 H, s), and 2.81 (3 H, s) (Found: C, 43.2; H, 3.6; N, 3.9. $C_{13}H_{13}ClNO_5PS$ requires C, 43.2; H, 3.6; N, 3.9%).

O-*Methylsulphonyl*-N-[*phenyl*(p-*cresyl*)*phosphinoyl*]*hydroxylamine* (**4**; X = NHOMs). This compound crystallised from aqueous methanol (63%), m.p. 154—156 °C (decomp.), *m/z* 341 (M^+, 10%); $\nu_{max.}$ (Nujol) 3 065 (NH) and 1 185 cm^{-1} (P = O); δ ($CDCl_3$) 8.12 (1 H, d, J_{PH} 7 Hz), 8.1—7.3 (5 H, m), 7.08 (4 H, s), 2.78 (3 H, s), and 2.27 (3 H, s) (Found: C, 49.4; H, 4.8; N, 4.0. $C_{14}H_{16}NO_5PS$ requires C, 49.3; H, 4.7; N, 4.1%).

N-[*Bis*(p-*chlorophenoxy*)*phosphinoyl*]-O-*methylsulphonylhydroxylamine* (**5**; X = NHOMs). This compound crystallised from dichloromethane—light petroleum (b.p. 60—80 °C) (80%), m.p. 128—129 °C, *m/z* 415,413, and 411 (M^+, 15%); $\nu_{max.}$ (Nujol) 3 110 (NH) and 1 190 cm^{-1} (P = O); δ ($CDCl_3$) 8.46 (1 H, d, J_{PH} 13 Hz), 7.45—7.0 (8 H, AA'BB' pattern centred at 7.22), and 3.07 (3 H, s) (Found: C, 37.65; H, 2.9; N, 3.4. $C_{13}H_{12}Cl_2NO_6PS$ requires C, 37.9; H, 2.9; N, 3.4%).

N-(*Di*-p-*cresylphosphinoyl*)-O-*methylsulphonylhydroxylamine* (**6**; X = NHOMs). This compound crystallised from methanol (64%), m.p. 136—138 °C, *m/z* 371 (M^+, 11%); $\nu_{max.}$ (Nujol) 3 075 (NH) and 1 190 cm^{-1} (P = O); δ ($CDCl_3$) 8.26 (1 H, d, J_{PH} 12 Hz), 7.06 (8 H, s), 3.03 (3 H, s), and 2.27 (6 H, s) (Found: C, 48.6; H, 4.9; N, 3.8. $C_{15}H_{18}NO_6PS$ requires C, 48.5; H, 4.9; N, 3.8%).

O-(p-*Nitrophenylsulphonyl*)-N-[*phenyl*(p-*chlorophenoxy*)*phosphinoyl*]*hydroxylamine* (**3**; X = NHONs). This compound crystallised from aqueous methanol (68%), m.p. 148—149 °C, *m/z* 470 and 468 (M^+, 5%); $\nu_{max.}$ (Nujol) 3 060 (NH) and 1 190 cm^{-1} (P = O); δ (CD_3OD) 8.4—6.95 (complex; includes two AA'BB' patterns centred at 8.06 and 7.17) (Found: C, 46.3; H, 3.0; N, 6.15. $C_{18}H_{14}ClN_2O_7PS$ requires C, 46.1; H, 3.0; N, 6.0%). The reaction time was reduced to 4 min in this case.

O-(p-*Nitrophenylsulphonyl*)-N-[*phenyl*(p-*cresyl*)*phosphinoyl*]*hydroxylamine* (**4**; X = NHONs). This compound recrystallised from benzene–light petroleum (b.p. 60—80 °C), m.p. 143 °C (decomp.), *m/z* 448 (M^+, 8%); $\nu_{max.}$ (Nujol) 3 075 (NH) and 1 195 cm^{-1} (P = O); δ (CD_3SOCD_3) 10.89 (1 H, d, J_{PH} 9 Hz), 8.3—7.9 (4H, AA'BB' pattern centred at 8.09), 7.9—7.3 (5 H, m), 7.15—6.8 (4 H, AA'BB' pattern centred at 6.94), and 2.20 (3 H, s) (Found: C, 51.0; H, 3.8; N, 6.1. $C_{19}H_{17}N_2O_7PS$ requires C, 50.9; H, 3.8; N, 6.25%). Initially this compound was crystallised from methanol when it formed a strong solvate

(M·CH_3OH) (84%), δ ($CDCl_3$) included 3.39 (3 H, s) and 1.35 (1 H, s); $\nu_{max.}$ (Nujol) included 3 320 cm^{-1} (OH) (Found: C, 50.0; H, 4.3; N, 5.8. $C_{19}H_{17}N_2O_7PS·CH_3OH$ requires C, 50.0; H, 4.4; N, 5.85%).

N-[*Bis*(p-*chlorophenoxy*)*phosphinoyl*]-O-(p-*nitrophenylsulphonyl*)*hydroxylamine* (**5**; X = NHONs). This compound was obtained initially as a complex with pyridine (83%). This was dissolved in chloroform and the solution was washed with aqueous HCl (1 mol equiv.), concentrated to a small volume, and cooled in ice to give the pure compound, m.p. 157—158 °C, *m/z* 522, 520, and 518 (M^+, 3%); $\nu_{max.}$ (Nujol) 3 100 (NH) and 1 190 cm^{-1} (P = O); δ ($CDCl_3$) 8.2—7.9 (4 H, AA'BB' pattern centred at 8.06), 7.76 (1 H, d, J_{PH} 12 Hz), and 7.3—6.85 (8 H, AA'BB' pattern centred at 7.09) (Found: C, 41.8; H, 2.6; N, 5.3. $C_{18}H_{13}Cl_2N_2O_8PS$ requires C, 41.6; H, 2.5; N, 5.4%). The reaction time was reduced to 5.5 min in this case.

N-(*Di*-p-*cresylphosphinoyl*)-O-(p-*nitrophenylsulphonyl*)*hydroxylamine* (**6**; X = NHONs). This compound (92% crude) crystallised from aqueous methanol, m.p. 142—144 °C (decomp.), *m/z* 478 (M^+, 5%); $\nu_{max.}$ 3 120 (NH) and 1 190 cm^{-1} (P = O); δ ($CDCl_3$) 8.2 (1 H, br), 7.96 (4 H, s), 7.1—6.75 (8 H, AA'BB' pattern centred at 6.90), and 2.24 (6 H, s) (Found: C, 50.1; H, 4.0; N, 6.0. $C_{20}H_{19}N_2O_8PS$ requires C, 50.2; H, 4.0; N, 5.9%). The reaction time was 7 min in this case.

Preparation of Authentic Samples for Comparison with Reaction Products.—N-[*Bis*(p-*chlorophenoxy*)*phosphinoyl*]-N'-*t-butylhydrazine* (**13**; Ar = *p*-chlorophenyl). A suspension of t-butylhydrazine hydrochloride (0.44 g, 3.5 mmol) in dichloromethane (6 ml) was stirred vigorously at 0 °C. A solution of triethylamine (0.35 g, 3.5 mmol) in dichloromethane (2 ml) was added dropwise, followed after 5 min by a solution of bis-*p*-chlorophenyl phosphorochloridate (0.50 g, 1.5 mmol) in dichloromethane (4 ml). After 0.5 h at room temperature the mixture was washed with water, dried (Na_2SO_4), and concentrated to give a solid. Crystallisation from benzene–light petroleum (b.p. 60—80 °C) afforded the *hydrazine* (**13**; Ar = *p*-chlorophenyl) (0.50 g, 86%), m.p. 126—127 °C, *m/z* 392, 390, and 388 (M^+, 30%); $\nu_{max.}$ (CCl_4) 3 200 (NH), 1 490, 1 200 (P=O), and 945 cm^{-1}; δ ($CDCl_3$) 7.18 (8 H, s), 5.07 (1 H, d, J_{PH} 36 Hz), 2.85 (1 H, br s), and 1.03 (9 H, s) (Found: C, 49.4; H, 5.0; N, 7.2. $C_{16}H_{19}Cl_2N_2O_3O$ requires C, 49.4; H, 4.9; N, 7.2%).

N-(*Di*-p-*cresylphosphinoyl*)-N'-*t-butylhydrazine* (**13**; Ar = *p*-tolyl). A similar preparation using di-*p*-tolyl phosphorochloridate gave the *hydrazine* (**13**; Ar = *p*-tolyl) (94%), crystallised from light petroleum (b.p. 60—80 °C), m.p. 96—98 °C, *m/z* 348 (M^+, 20%); $\nu_{max.}$ (Nujol) 3 190 (NH), 1 500, 1 250, 1 220, 1 190, and 1 165 cm^{-1}; δ ($CDCl_3$) 7.04 (8 H, s), 4.84 (1 H, d, J_{PH} 35 Hz), 2.97 (1 H, br), 2.26 (6 H, s), and 1.03 (9 H, s) (Found: C, 61.8; H, 7.2; N, 8.15. $C_{18}H_{25}N_2O_3P$ requires C, 62.05; H, 7.2; N, 8.0%).

p-*Chlorophenyl* N-*phenyl*-N'-*t-butylphosphorodiamidate* (**7**; Ar = *p*-chlorophenyl). Aniline (0.56 g, 6.0 mmol) in ether (3 ml) was added dropwise to a stirred solution of *p*-chlorophenyl phosphorodichloridate[9] (0.74 g, 3.0 mmol) in ether (2 ml) at 0 °C. After 1 h at room temperature further solvent was added and the mixture was heated to boiling and filtered (to remove $PhNH_3Cl$). The filtrate was concentrated and the residue crystallised from benzene to give p-*chlorophenyl* N-*phenylphosphoramidochloridate* (0.59 g, 65%), m.p. 149—151 °C (rapid heating), *m/z* 305, 303, and 301 (M^+, 50%) (not obtained analytically pure). To a portion of this material (0.12 g, 0.40 mmol) suspended in benzene, was added t-butylamine (0.25 ml), and the mixture was heated at 65 °C for 0.7 h. Solid (Bu^tNH_3Cl) was filtered off and the filtrate was evaporated to dryness. Crystallisation of the residue from light petroleum (b.p. 40—60 °C) gave p-*chlorophenyl* N-*phenyl*-N'-*t-butylphosphorodiamidate* (**7**; Ar = *p*-chlorophenyl) (0.09 g, 68%), m.p. 115.5—116.5 °C (after melting and resolidifying at 95 °C), *m/z* 340 and 338 (M^+, 45%); $\nu_{max.}$ (Nujol) 3 380, 3 270br (NH), and 1 210 cm^{-1} (P = O); δ ($CDCl_3$) 7.3—6.8 (9 H, m), 6.36 (1 H, d, J_{PH} 8 Hz), 2.93 (1 H, d, J_{PH} 9 Hz), and 1.26 (9 H, s) (Found: C, 56.9; H, 5.9; N, 8.2; P, 8.75. $C_{16}H_{20}ClN_2O_2P$ requires C, 56.7; H, 5.95; N, 8.3; P, 9.1%).

Reactions of N-*Phosphonoyl*-O-*sulphonylhydroxylamines with t-Butylamine.*—(*a*). The phenyl (*p*-cresyl) compound (**4**; X = NHOMs) (0.40 g, 1.17 mmol) was stirred with t-butylamine (2.0 ml) and dichloromethane (3 ml) at room temperature. Over 4.5 h, the ^{31}P n.m.r. signal δ_P 23.6 was gradually replaced by δ_P 1.6 (56%) and −6.0 (27%) (and smaller peaks δ_P 21.0, 15.1, and 12.1). Volatile matter was evaporated and the residue was partitioned between dichloromethane and water. The organic layer contained a single phosphorus compound (δ_P 1.6) and a product identified as *N*-t-butylmethanesulphonamide (25%) by comparison of its ^1H n.m.r. signals [δ(CCl_4) 2.85(s) and 1.29 (s)] and R_F value (0.21 on alumina, ether eluant) with those of an authentic sample [m.p. 40—41 °C (lit.,[10] 40—41 °C)] prepared from methanesulphonyl chloride and t-butylamine. This mixture was dissolved in light petroleum (b.p. 60—80 °C) and the solution was stored at −40 °C; an oil gradually separated and slowly solidified. Recrystallisation from aqueous methanol afforded p-*tolyl* N-*phenyl*-N'-*t-butylphosphorodiamidate* (**7**; Ar = *p*-tolyl) (0.20 g, 54%), m.p. 106—108 °C, *m/z* 318 (M^+, 55%), 303 (M^+ − Me, 100), and 262 (M^+ − C_4H_8, 10); $\nu_{max.}$ (Nujol) 3 360, 3 135 (NH), 1 240, 1 215, and 1 200 cm^{-1} (P = O); δ ($CDCl_3$) 7.25—6.75 (9 H, m), 6.42 (1 H, d, J_{PH} 9 Hz), 2.91 (1 H, d, J_{PH} 8 Hz), 2.19 (3 H, s), and 1.25 (9 H, s) (Found: C, 63.5; H, 7.1; N, 8.8. $C_{17}H_{23}N_2O_2P$ requires C, 64.1; H, 7.3; N, 8.8%). The aqueous layer was evaporated to dryness and the principal component identified as the t-butylammonium salt of hydrogen *p*-tolyl *N*-phenylphosphoramidate (**9**; Ar = *p*-tolyl) by comparison of its ^1H n.m.r. signals [especially δ ($CDCl_3$) 5.56 (d, J_{PH} 8 Hz, NH) and 2.20 (s, MeC_6H_4O)] with those of the material prepared below, and enhancement of its ^{31}P n.m.r. signal (δ_P − 6.0).

Hydrogen p-*tolyl* N-*phenylphosphoramidate* (**9**, Ar = *p*-tolyl). This was obtained by hydrolysis of *p*-tolyl *N*-phenylphosphorochloramidate (NaOH in aqueous tetrahydrofuran; the product was precipitated by acidification with HCl) and also by rearrangement of the hydroxylamine derivatives (**4**; X = NHOMs) and (**4**; X = NHONs) in aqueous media (NaOH added to suspensions in H_2O; products precipitated by acidification with HCl). It had m.p. 122—124 °C, *m/z* 263 (M^+, 20%); $\nu_{max.}$ (Nujol) 3 220 (NH), 2 640 br, 2 280 br (OH), and 1 205 cm^{-1} (P = O) (Found: C, 59.6; H, 5.4; N, 5.5. $C_{13}H_{14}NO_3P$ requires C, 59.3; H, 5.4; N, 5.3%).

(*b*) The phenyl (*p*-cresyl) compound (**4**; X = NHONs) (0.50 g, 1.11 mmol) reacted almost immediately with t-butylamine (2.0 ml) in dichloromethane (2 ml) at 0 °C, and the ^{31}P n.m.r. spectrum of the reaction mixture consisted of a single peak (δ_P 1.4). The product was isolated by chromatography (to remove *p*-nitrobenzenesulphonate) and crystallisation from aqueous methanol, and was identified as *p*-tolyl *N*-phenyl-*N'*-t-butylphosphorodiamidate (**7**; Ar = *p*-tolyl) (0.26 g, 73%), m.p. 106—108 °C, spectra as for the sample obtained in (*a*).

(*c*) In an experiment similar to (*a*) the phenyl (*p*-chlorophenoxy) compound (**3**; X = NHOMs) was treated with t-butylamine. The organic layer from the work-up was examined by g.l.c. (3% OV 17); comparison with authentic samples showed the presence of *p*-chlorophenol (R_t 3.8 min at 140 °C) and *p*-chlorophenyl *N*-phenyl-*N'*-t-butylphosphorodiamidate (**7**; Ar = *p*-chlorophenyl) (R_t 12.6 min at 240 °C) (each *ca.* 20% yield). The ^1H n.m.r. spectrum also suggested the presence of these two compounds, and in addition a comparable yield of *N*-t-butylmethanesulphonamide. In a

control experiment an authentic sample of the phosphorodiamidate suffered no appreciable decomposition by t-butylamine over 22 h at room temperature.

(*d*) The phenyl (*p*-chlorophenoxy) compound (**3**; X = NHONs) (0.083 g, 0.18 mmol) was mixed with t-butylamine (0.8 ml) at 0 °C. After 1 h at room temperature volatile matter was evaporated and the residue, dissolved in chloroform, was washed with water. The solvent was removed and the product was isolated by extraction into hot light petroleum (b.p. 60—80 °C); on cooling, crystals of *p*-chlorophenyl *N*-phenyl-*N'*-t-butylphosphorodiamidate (**7**; Ar = *p*-chlorophenyl) (0.046 g, 77%) were obtained; m.p. 115—117 °C, R_t and spectra identical to those of the authentic sample. No *p*-chlorophenol was detected.

Reactions of N-*Phosphoroyl*-O-*sulphonylhydroxylamines with t-Butylamine.*—(*a*) The di-*p*-cresyl compound (**6**; X = NHOMs) (0.50 g, 1.35 mmol) was dissolved in dichloromethane (2 ml) at 0 °C. On addition of t-butylamine (2.0 ml) the signal δ_P − 5.0 was replaced by δ_P 9.8 and this in turn was gradually replaced by δ_P 2.2 (66%), −7.3 (15%), and −12.1 (18%) over 72 h at room temperature. Volatile matter was evaporated and the residue was partitioned between dichloromethane and water. The organic layer contained the product δ_P 2.2; crystallisation from ether–light petroleum (b.p. 60—80 °C) gave di-*p*-tolyl phosphoramidate (**6**; X = NH_2) (0.155 g, 42%), m.p. 135—137 °C, *m/z* 277 (M^+, 100%), 276 (40), and 198 (40); $\nu_{max.}$ (Nujol) 3 430, 3 240 (NH), 1 255, and 1 230 cm^{-1} (P = O); δ ($CDCl_3$) 7.07 (8 H, s), 3.41 (2 H, br d, J_{PH} 6 Hz), and 2.26 (6 H, s), the identity of which was confirmed by comparison with an authentic sample prepared from di-*p*-tolyl phosphorochloridate and ammonia. Of the products in the water layer, one (δ_P − 12.1) was apparently di-*p*-tolyl hydrogen phosphate (as its t-butylammonium salt) since its ^{31}P n.m.r. signal increased in intensity when authentic material was added; the other was not identified. (The substrate used in this experiment seems to form a reasonably stable salt with base, *e.g.* it dissolved in water when sodium hydroxide was added and was precipitated unchanged on acidification after 10 min.)

(*b*) The di-*p*-cresyl compound (**6**; X = NHONs) (0.070 g) was dissolved in t-butylamine (1.1 ml) at room temperature. Over a period of 4 h δ_P 9.3 was replaced by δ_P − 0.7 (70%) and several small peaks [including δ_P 2.3 (8%) assigned to di-*p*-tolyl phosphoramidate]. Volatile matter was evaporated and the residue, dissolved in chloroform, was washed with water. Removal of the solvent and extraction of the product into hot light petroleum (b.p. 60—80 °C) afforded the compound δ_P − 0.7. After crystallisation from ether–light petroleum (b.p. 60—80 °C) this had ^1H n.m.r., i.r., and mass spectra identical with those of an authentic sample of *N*-(di-*p*-cresylphosphinoyl)—*N'*-t-butylhydrazine (**13**; Ar = *p*-tolyl).

(*c*) In an experiment similar to (*b*) the bis(*p*-chlorophenoxy) light petroleum (b.p. 60—80 °C) afforded the compound δ_P 10.3 was replaced over a period of 1 h by δ_P 2.4 and −0.8 (*ca.* 30% each) and four smaller peaks (*ca.* 10% each). Work-up as above afforded the product δ_P − 0.8 which after crystallisation from light petroleum (b.p. 60—80 °C) had ^1H n.m.r., i.r., and mass spectra identical with those for an authentic sample of *N*-[bis(*p*-chlorophenoxy) phosphinoyl-*N'*-t-butyl]hydrazine (**13**; Ar = *p*-chlorophenyl).

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