Migration of the Amino Group in the Base-induced Rearrangements of *N*-(Aminophosphinoyl)-*O*-sulphonylhydroxylamines

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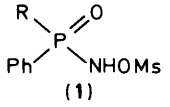
The *N*-phosphinoylhydroxylamines $R^1R^2P(O)NHOH$ having $R^1 = R^2 = PhNH$; $R^1 = Ph$, $R^2 = PhNH$; and $R^1 = Ph$, $R^2 = Me_2N$ have been prepared and converted into their *O*-methylsulphonyl derivatives. The methanesulphonates rearrange in methanol containing sodium methoxide or pyridine, an amino group (PhNH or Me_2N) migrating from phosphorus to nitrogen. These reactions are much faster than the analogous reactions of $Ph_2P(O)NHOMs$ involving migration of a Ph group, and with the unsymmetrical substrates migration of the amino group occurs to the complete exclusion of phenyl migration.

While the chemistry of *N*-phosphinoylhydroxylamines is still relatively unexplored, it is clear that their *O*-sulphonyl derivatives generally undergo a Lossen-like rearrangement with base.[1,2] Thus the methanesulphonates (**1**) react with NaOMe–MeOH or t-butylamine to give the rearrangement products (**3**; Y = MeO or Bu^{t}NH) derived from the monomeric metaphosphonimidates (**2**).[1,2] When the group R in compound (**1**) is a substituted phenyl, competitive migration of R and Ph leads to a mixture of the two possible rearrangement products,[3] but when R is alkyl[2] or aryloxy[4] only the phenyl group migrates. Rearrangement is not observed with the diaryloxy compounds $(ArO)_2P(O)NHOMs$.[4] The non-migration of groups attached *via* an oxygen atom to the phosphoryl centre prompts the question of what would happen if the oxygen were to be replaced by nitrogen. The present work addresses that question.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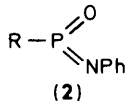
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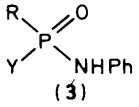
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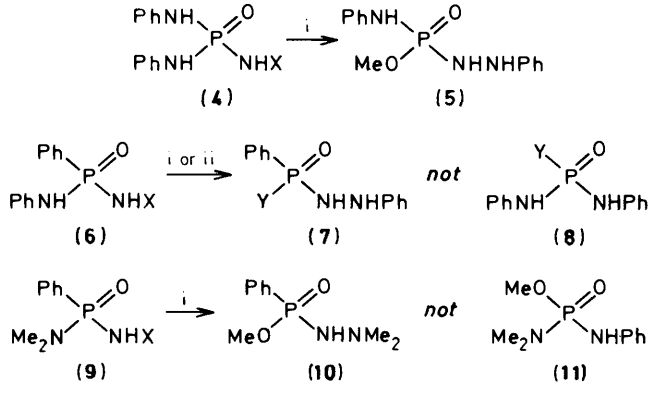
Results and Discussion

The phosphinoylhydroxylamines (**4**), (**6**), and (**9**) (X = OH) were prepared by treatment of the corresponding phosphinoyl chlorides with *O*-trimethylsilylhydroxylamine followed by removal of the silyl blocking group with methanol or water. They decomposed at (or below) the m.p., but were obtained pure by careful crystallisation. With methanesulphonyl chloride in pyridine at $\leqslant 0$ °C they were readily converted into the *O*-methylsulphonyl derivatives. Of these (**4**) and (**6**) (X = OMs) were obtained as reasonably stable crystalline solids, showing in their ^{1}H n.m.r. spectra the expected lowfield phosphorus-coupled doublet (δ 10.2 or 10.5, J_{PH} 10 Hz) for the proton of the NHOMs moiety; attempts to isolate the dimethylamino compound (**9**; X = OMs) were unsuccessful, resulting in decomposition.

When the dianilino methanesulphonate (**4**; X = OMs) (δ_P 4.5) was dissolved in methanol and treated with sodium methoxide (1 equiv.) it was immediately and cleanly transformed into a product having δ_P 10.1. Evidence that this was the rearrangement product (**5**) included: (i) peaks in the mass spectrum for the molecular ion (M^+ 277) and for an $(M - 2)^+$ ion corresponding to loss of H_2, and (ii) ^{1}H n.m.r. signals attributable to a *P*-methoxy group (δ 3.75, J_{PH} 11 Hz) and three NH protons. One of the NH protons (δ 5.0) showed a remarkably large coupling to phosphorus (J_{PH} 32 Hz), as seems often to be the case with P(O)NHN systems.[5]

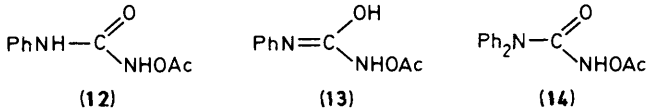
The unsymmetrical methanesulphonate (**6**; X = OMs) (δ_P 18.6) also gave a single product (δ_P 24.2) with methoxide (1 equiv.), even though in principle rearrangement could now occur with migration of either the Ph or PhNH group. In fact it was clear that the product was the hydrazine (**7**; Y = MeO) resulting from migration of the PhNH group, since the ^{1}H n.m.r. spectrum included signals for a phenyl group still attached directly to phosphorus and for an NH with a very large coupling to phosphorus (J_{PH} 27 Hz), while the mass spectrum contained both M^+ and $(M - 2)^+$ peaks. An authentic specimen was used to show that none of the alternative phenyl-migration product (**8**; Y = MeO) (δ_P 4.8) had been formed in the rearrangement (1% would have been detected).

When treated with t-butylamine, a much weaker base, in dichloromethane, the unsymmetrical substrate (**6**; X = OMs) again rearranged rapidly. The major product (δ_P 18.9) was the hydrazine (**7**; Y = Bu^{t}NH) (δ 4.8, d, J_{PH} 22 Hz, NH), but now it was accompanied by a second product (δ_P 13.9). Although the yield of the hydrazine (**7**; Y = Bu^{t}NH) was rather variable (75—90% by ^{31}P n.m.r.; 70% isolated) it was easily purified because the minor product was completely removed by washing with water. This was apparently the t-butylamine salt of the acid (**7**; Y = OH), also a product of PhNH migration, since the same compound (identical ^{1}H and ^{31}P n.m.r. spectra in CD_3OD) was obtained when the methanesulphonate (**6**; X = OMs) was treated with aqueous t-butylamine. As with methoxide, there seems to be exclusive migration of the PhNH group, and no trace of the product (**8**; Y = Bu^{t}NH) that would have resulted from phenyl migration could be detected (δ_P − 0.8 for an authentic sample).


(4) (5) (6) (7) (8) (9) (10) (11)

Scheme 1. *Reagents:* i MeOH, NaOMe or pyridine; ii Bu^{t}NH$_2$

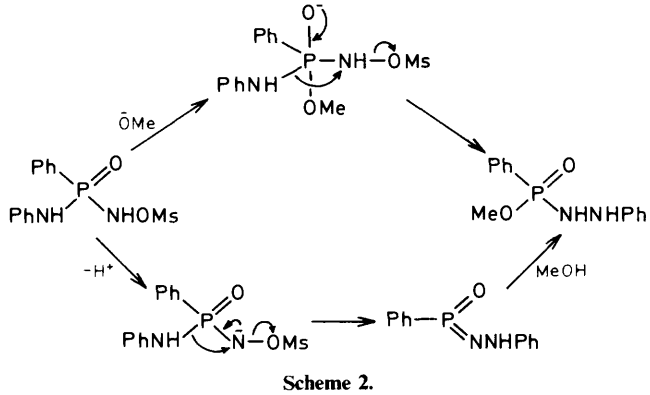
The ready migration of the PhNH group in these reactions is in sharp contrast to what has been observed for related carbonyl compounds. In particular, Hurd found no evidence for Lossen rearrangement of the hydroxamic acid derivative (**12**) in aqueous alkali, although both the diphenylamino compound (**14**) and its diethylamino analogue rearranged rapidly at room temperature.[6] It was thought that the failure of compound (**12**) to rearrange might stem from a preference for existence in the tautomeric form (**13**).[6]



(**12**) (**13**) (**14**)

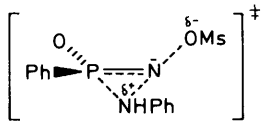
Because the dimethylamino methanesulphonate (**9**; X = OMs) decomposed on attempted isolation, the concentrated pyridine solution (*ca.* 0.1 ml) from its preparation was diluted with methanol (1.0 ml) and subsequent changes were monitored by ^{31}P n.m.r. spectroscopy. Over a period of 20—25 min the peak at δ_P 28.6 was replaced by δ_P 22.4 (75—95%) and δ_P 15.3 (5—20%). The principal product was isolated and characterised. The ^1H n.m.r. spectrum showed that the Ph group was still attached directly to phosphorus but the Me_2N group (δ 2.34, 6 H, s) was not, while the NH signal showed a large coupling to phosphorus (J_{PH} 27 Hz). These data clearly point to the hydrazine structure (**10**) derived from migration of the Me_2N group. An authentic sample of the product (**11**) (δ_P 13.1) that would have resulted from phenyl migration was prepared and used to prove that it had not been formed in the rearrangement (1% would have been detected).

The two anilino methanesulphonates (**4**) and (**6**) (X = OMs) also rearranged quite readily in methanol when pyridine (*ca.* 10% v/v) was used as the base, their half-lives being *ca.* 70 min at 27 °C compared with 6 min for the dimethylamino compound. By contrast, the rearrangement of $Ph_2P(O)NHOMs$ was extremely slow under these conditions, being only 12% complete after 67 h (estimated $t_{0.5}$ *ca.* 15 days).



Scheme 2.

In none of the foregoing reactions were metaphosphonimidate intermediates detected, but that does not constitute evidence against their involvement. Like monomeric metaphosphate[7] they contain three-co-ordinate P^V; they will therefore be powerful electrophiles, and will react very rapidly with nucleophiles such as methanol. On the other hand, the high reactivity of the substrates relative to $Ph_2P(O)NHOMs$ surely is strong evidence against the most plausible alternative mechanism. That involves nucleophilic attack on the substrate (*e.g.* Scheme 2, upper pathway) and collapse of the resulting phosphorane to product. Replacing a Ph group by PhNH or Me_2N would retard nucleophilic attack at phosphorus, not accelerate it.[8] In the metaphosphonimidate mechanism (*e.g.* Scheme 2, lower pathway) the enhanced reactivity could be due to an increase in the acidity of the NHOMs proton, but this seems not to be the principal factor. As noted above, replacing one of the Ph groups in $Ph_2P(O)NHOMs$ by PhNH causes a large (*ca.* 300-fold) increase in rate but replacing the second has no additional effect. Also, the Me_2N group increases the rate substantially more than does PhNH. It therefore seems that the enhanced reactivity is mainly a result of much greater migratory aptitudes for the PhNH and Me_2N groups relative to Ph. This would also, of course, explain the complete lack of Ph migration in the reactions of the unsymmetrical substrates. Moreover, it is consistent with previous indications that the migrating group has to accommodate substantial positive charge in the rearrangement transition state *e.g.* (**15**).[3]



(**15**)

Experimental

Instrumentation was as previously described.[1] ^{31}P N.m.r. chemical shifts are reported relative to external 85% H_3PO_4, with positive values at lower field. Quoted i.r. frequencies are for spectra recorded as Nujol mulls. Light petroleum refers to the fraction b.p. 60—80 °C. Pyridine was dried over potassium hydroxide and distilled. *O*-Trimethylsilylhydroxylamine was prepared as before.[1] All hydroxylamine derivatives were assumed to be of limited stability; during their recrystallisation heating was kept gentle and brief, and they were stored at −20 °C. Evaporation of volatile material was always carried out under reduced pressure with only minimal warming. Solids were dried at room temperature over phosphoric anhydride at 0.3 mmHg.

N-(Dianilinophosphinoyl)hydroxylamine (**4**; X = OH).—Solid *NN'*-diphenylphosphorodiamidic chloride[9] (1.60 g, 6.00 mmol) was stirred at 0 °C in a flask fitted with a serum cap. Pyridine (2.1 ml) was added, followed by *O*-trimethylsilylhydroxylamine (0.95 g, 9.0 mmol), and the mixture was then stirred at room temperature for 2 h. Desilylation was accomplished by treatment with methanol (2.0 ml) for 0.25 h, pumping off volatile material, adding iced water (70 ml), and stirring at 0 °C for 1.5 h. The resulting solid was filtered off, washed with water, and dried. The crude product (1.34 g, 85%), m.p. 132—133 °C (decomp.), was purified by dissolution in warm methanol (10 ml), concentration of the solution to a small volume, and addition of ether (30 ml) to give the *hydroxylamine* (**4**; X = OH) (1.02 g, 65%), m.p. 132—134 °C (decomp.), *m/z* 263 (M^+, 4%) and 93 (100); $\nu_{max.}$ 3 340, 3 290, and 3 175 br cm^{-1}, δ_P(MeOH) 8.3, δ[$(CD_3)_2SO$] 7.92 (1 H, d, J_{PH} 5 Hz), 7.53 (1 H, d, J_{PH} 16 Hz), 7.34 (2 H, d, J_{PH} 10 Hz), and 7.25—6.6 (10 H, m) (Found: C, 55.05; H, 5.35; N, 16.2; P, 11.6. $C_{12}H_{14}N_3O_2P$ requires C, 54.75; H, 5.4; N, 16.0; P, 11.8%).

N-[Anilino(phenyl)phosphinoyl]hydroxylamine (**6**; X = OH).—*NP*-Diphenylphosphonamidic chloride[10] (1.25 g, 5.00 mmol) was mixed with pyridine (2 ml) and *O*-trimethylsilylhydroxylamine (0.79 g, 7.50 mmol) as above, and the viscous solution was stirred for 25 min at 0 °C. Methanol (2 ml) was added, the cooling bath removed, and desilylation allowed to

proceed for 10 min. The mixture was concentrated to two-thirds of its original volume and was then added with vigorous stirring to ice–water (40 ml). The oil that separated became a fine solid during 1 h. The solid was filtered off, washed with water and then ether, and dried to give the *hydroxylamine* (**6**; X = OH) (0.99 g, 80%); δ_P(MeOH) 21.2. A sample crystallised from ethanol–water had m.p. 110—111 °C (decomp.); $\nu_{max.}$ 3 230 and 3 180 cm^{-1}; δ[$(CD_3)_2SO$] 8.1—7.3 (7 or 8 H, m; includes 8.00, d, J_{PH} 6 Hz and 7.76, d, J_{PH} 14 Hz), and 7.2—6.6 (5 H, m) (Found: C, 58.4; H, 5.3; N, 11.3; P, 12.2. $C_{12}H_{13}N_2O_2P$ requires C, 58.1; H, 5.3; N, 11.3; P, 12.5%).

N-[*Dimethylamino(phenyl)phosphinoyl*]*hydroxylamine* (**9**; X = OH).—*NN*-Dimethyl-*P*-phenylphosphonamidic chloride[11] (1.73 g, 8.5 mmol) (δ_P 41.3) in dichloromethane (5 ml) was added with stirring to a solution of *O*-trimethylsilylhydroxylamine (0.92 g, 8.8 mmol) and triethylamine (0.89 g, 8.8 mmol) in dichloromethane (8 ml) at 0 °C. Stirring was continued until ^{31}P n.m.r. spectroscopy showed reaction to be complete (δ_P 28.4) (8.5 h at 0 °C). Methanol (1.7 ml) was added and desilylation was allowed to proceed overnight at 0 °C. Volatile material was evaporated and the residue, dissolved in dichloromethane (50 ml), was washed with iced water (7 ml). (The product is soluble in water, and some was lost in the washing). Most of the solvent was evaporated and ether was added to give the solid product (0.90 g) contaminated with Et_3N·HCl. A pure sample of the *hydroxylamine* (**9**; X = OH) was obtained by washing the crude solid with a very small volume of iced water and recrystallising from dichloromethane–ether. It had m.p. 110—112 °C (decomp.), *m/z* 200 (M^+, 8%) and 168 (100); $\nu_{max.}$ 3 260 and 3 220 cm^{-1}; δ_P(MeOH) 29.8, $\delta(CDCl_3)$ *ca.* 8.0 br (1 H), 7.95—7.25 (5 H, m), 6.35 (1 H, d, J_{PH} 15 Hz), and 2.65 (6 H, d, J_{PH} 10 Hz) (Found: C, 47.9; H, 6.5; N, 14.0. $C_8H_{13}N_2O_2P$ requires C, 48.0; H, 6.5; N, 14.0%).

N-(*Dianilinophosphinoyl*)-O-*methylsulphonylhydroxylamine* (**4**; X = OMs).—The phosphinoylhydroxylamine (**4**; X = OH) (158 mg, 0.60 mmol) was mixed with pyridine (0.25 ml) at −5 °C and methanesulphonyl chloride (97 mg, 0.85 mmol) was added immediately. Stirring and cooling were continued for 4 min, and iced water (4 ml) was then added. After mixing thoroughly, the water was decanted off and the sticky residue was triturated with cold methanol (0.8 ml) to give a solid. Iced water (8 ml) was added and the solid was filtered off and dried. The crude product (195 mg, 95%) was spectroscopically pure, δ_P(MeOH) 4.5, but slightly coloured. It was dissolved in warm acetone ($T \leqslant 40$ °C) and the solution was diluted with an equal volume of light petroleum. On cooling, crystals of the *methanesulphonate* (**4**; X = OMs) (145 mg, 71%) were obtained, *m/z* 341 (M^+, 10%) and 79 (100); $\nu_{max.}$ 3 340, 3 240 and 3 165 br cm^{-1}; δ_P(MeOH) 8.2, δ[$(CD_3)_2SO$] 10.18 (1 H, d, J_{PH} 10 Hz), 7.86 (2 H, d, J_{PH} 11 Hz), 7.25—6.7 (10 H, m), and 3.09 (3 H, s). A sample recrystallised from aqueous methanol had m.p. 78—79 °C (Found: C, 45.5; H, 5.0; N, 11.9. $C_{13}H_{16}N_3O_4PS$ requires C, 45.7; H, 4.7; N, 12.3%).

N-[*Anilino(phenyl)phosphinoyl*]-O-*methylsulphonylhydroxylamine* (**6**; X = OMs).—The phosphinoylhydroxylamine (**6**; X = OH) (300 mg, 1.21 mmol) was stirred with pyridine (0.4 ml) and methanesulphonyl chloride (280 mg, 2.42 mmol) at 0 °C for 8 min. Iced water (15 ml) was added and stirring was continued at 0 °C until the initial oil was transformed into a fine solid. This was filtered off, washed with water and then chloroform–ether (1:1), and dried to give the *methanesulphonate* (**6**; X = OMs) (258 mg, 65%). A sample crystallised from methanol–water had m.p. 125 °C (decomp.) (rapid heating), $\nu_{max.}$ 3 330 and 3 030 br cm^{-1}, δ_P(MeOH) 18.6, δ[$(CD_3)_2SO$] 10.52 (1 H, d, J_{PH} 10 Hz), 8.08 (1 H, d, J_{PH} 14 Hz), 8.0–7.35 (5 H, m), 7.3—6.75 (5 H, m), and 3.18 (3 H, s) (Found: C, 47.9; H, 4.6; N, 8.7; P, 9.4. $C_{13}H_{15}N_2O_4PS$ requires C, 47.85; H, 4.6; N, 8.6; P, 9.5%).

N-[*Dimethylamino(phenyl)phosphinoyl*]-O-*methylsulphonylhydroxylamine* (**9**; X = OMs).—The phosphinoylhydroxylamine (**9**; X = OH) (50 mg, 0.25 mmol) was mixed with pyridine (0.10—0.15 ml) and methanesulphonyl chloride (44 mg, 0.38 mmol) at −5 °C for 8 min. The pyridine solution of the methanesulphonate (**9**; X = OMs), δ_P(MeOH) 28.6 (*ca.* 95%), was used immediately (see below). Attempts to isolate the methanesulphonate resulted in decomposition.

Reactions of N-*Phosphinoyl*-O-*sulphonylhydroxylamines*.—(*a*) The anilino(phenyl) methanesulphonate (**6**; X = OMs) (49 mg, 0.15 mmol) was dissolved in methanol (1.1 ml). Addition of methanolic sodium methoxide (1 equiv. of 2 M solution) immediately transformed it into a single product, δ_P(MeOH) 24.2. The solvent was evaporated and the residue was partitioned between dichloromethane and water. From the organic layer there was obtained, after crystallisation from dichloromethane-ether, *N*-phenyl-*N'*-[phenyl(methoxy)phosphinoyl]-hydrazine (**7**; Y = MeO) (34 mg, 86%), m.p. 142—143 °C (lit.,[12] 137—138 °C), *m/z* 262 (M^+, 15%), 260 (7), and 155 (100); $\nu_{max.}$ 3 295, 3 270, and 3 175 cm^{-1}; $\delta(CDCl_3)$ 8.0—7.3 (5 H, m), 7.3—6.65 (5 H, m), 5.32 (1 H, s, NH), 5.15 (1 H, d, J_{PH} 27 Hz, NH), and 3.71 (3 H, d, J_{PH} 11 Hz, OMe). The absence of methyl *NN'*-diphenylphosphorodiamidate (**8**; Y = MeO), δ_P(MeOH) 4.8, was established using an authentic sample prepared from *NN'*-diphenylphosphorodiamidic chloride and sodium methoxide. This had m.p. 124—125 °C (from dichloromethane–light petroleum) (lit.,[13] 108—109 °C or[14] 123 °C), *m/z* 262 (M^+, 55%); $\delta(CDCl_3)$ 7.25—6.85 (10 H, m), 6.05 (2 H, d, J_{PH} 9 Hz, NH), and 3.74 (3 H, d, J_{PH} 12 Hz).

(*b*) In a similar experiment the dianilino methanesulphonate (**4**; X = OMs) gave with methanolic sodium methoxide a single product, δ_P(MeOH) 10.1. Crystallisation from chloroform–ether afforded N-*phenyl*-N'-[*anilino(methoxy)phosphinoyl*]-*hydrazine* (**5**), m.p. 151.5—152.5 °C, *m/z* 277 (M^+, 10%), 275 (10), 170 (80), and 93 (100); $\nu_{max.}$ 3 335 and 3 260 cm^{-1}; $\delta(CDCl_3)$ 7.35—6.65 (10 H, m), 5.34 (2 H, br s, NH), 5.00 (1 H, d, J_{PH} 32 Hz, NH), and 3.75 (3 H, d, J_{PH} 11 Hz, OMe) (Found: C, 55.4; H, 5.7; N, 14.9%; M^+ 277.0974. $C_{13}H_{16}N_3O_2P$ requires C, 56.3; H, 5.8; N, 15.2%; *M* 277.0980).

(*c*) The pyridine solution of the dimethylamino(phenyl)-methanesulphonate (**9**; X = OMs) prepared above was diluted with methanol (1.0 ml). During *ca* 0.4 h the substrate was converted into products having δ_P(MeOH) 22.4 (75–95%) and 15.3 (5—20%) (the ratio varied between experiments). Volatile material was pumped off, the residue was partitioned between water and chloroform, and the major product was extracted from chloroform into dilute hydrochloric acid. The acid solution was neutralised and extracted with chloroform to give NN-*dimethyl*-N'-[*methoxy(phenyl)phosphinoyl*]*hydrazine* (**10**) which, after crystallisation from ether–light petroleum, had m.p. 82—85 °C, *m/z* 214 (M^+, 1%), 172 (40), 170 (40), 155 (30), and 59 (100); $\nu_{max.}$ 3 160 cm^{-1}; $\delta(CDCl_3)$ 8.0—7.25 (5 H, m), 4.04 (1 H, d, J_{PH} 27 Hz, NH), 3.71 (3 H, d, J_{PH} 11 Hz, OMe), and 2.34 (6 H, s, NMe_2) (Found: C, 50.5; H, 7.0; N, 13.1. $C_9H_{15}N_2O_2P$ requires C, 50.5; H, 7.1; N, 13.1%). The minor product was not identified, but the absence of *methyl* NN-*dimethyl*-N'-*phenylphosphorodiamidate* (**11**), δ_P(MeOH) 13.1, was proven using an authentic sample. This was prepared from *p*-methoxyphenyl *N*-phenylphosphoramidochloridate by sequential displacement of chloride by dimethylamine and *p*-methoxyphenol by methoxide (conc. NaOMe in MeOH, 80 °C, 4 h). It was purified by distillation, b.p. 150 °C (oven temp.) at 0.4 mmHg, followed by crystallisation from ether–light petroleum; m.p. 91—93 °C, *m/z*

214 (M^+, 70%) and 93 (100); $\nu_{max.}$ 3 195 and 3 170 cm^{-1}; $\delta(CDCl_3)$ 7.3—6.7 (5 H, m), 5.80 (1 H, br d, J_{PH} 7 Hz, NH), 3.67 (3 H, d, J_{PH} 11 Hz, OMe), and 2.68 (6 H, d, J_{PH} 10 Hz, NMe_2) (Found: C, 50.5; H, 7.0; N, 13.1. $C_9H_{15}N_2O_2P$ requires C, 50.5; H, 7.1; N, 13.1%).

(d) The anilino(phenyl) methanesulphonate (**6**; X = OMs) was suspended in dichloromethane. Addition of t-butylamine (10 mol equiv.) gave, within 1 min, a clear solution of two products, δ_P 18.9 (75—90%) and 13.9 (10—25%). Volatile material was evaporated off and the residue was partitioned between chloroform and water. The organic portion was concentrated and ether was added; this afforded N-*phenyl*-N'-[*phenyl*(*t-butylamino*)*phosphinoyl*]*hydrazine* (**7**; Y = Bu^tNH) (70%), m.p. 154—156 °C, *m/z* 303 (M^+, 6%), 196 (55), and 140 (100); $\nu_{max.}$ 3 330 br, 3 240, and 3 180 cm^{-1}; $\delta(CDCl_3)$ 7.95—7.2 (5 H, m), 7.2—6.65 (5 H, m), 5.84 (1 H, s, NH), 4.81 (1 H, d, J_{PH} 22 Hz, NH), 2.78 (1 H, d, J_{PH} 8 Hz, NH), and 1.22 (9 H, s, Bu^t) (Found: C, 63.2; H, 7.2; N, 13.9. $C_{16}H_{22}N_3OP$ requires C, 63.35; H, 7.3; N, 13.85%). The aqueous portion was evaporated to dryness and dissolved in CD_3OD, δ_P 14.2. The ^1H n.m.r. spectrum was dominated by peaks due to t-butylammonium methanesulphonate but also contained peaks at $\delta(CD_3OD)$ 7.9—7.2 (P–Ph) and 7.1—6.5 (NDNDPh). Exactly the same n.m.r. signals were observed for the product obtained when a suspension of (**6**; X = OMs) in water was treated with t-butylamine. This product is apparently the t-butylamine salt of the acid (**7**; Y = OH).

The absence of *N*-t-butyl-*N'N''*-diphenylphosphoric triamide (**8**; Y = Bu^tNH), $\delta_P(CH_2Cl_2)$ −0.8, was established using an authentic sample prepared by reaction of *NN'*-diphenylphosphorodiamidic chloride with t-butylamine. The *triamide* had m.p. 142 °C (softens at 135 °C) after crystallisation from aqueous methanol and prolonged drying at 50 °C, *m/z* 303 (M^+, 50%), 288 (40), and 93 (100); $\nu_{max.}$ 3 370 and 3 210 br cm^{-1}; $\delta(CDCl_3)$ 7.25—6.75 (10 H, m), 5.55 br (2 H, d, J_{PH} 6 Hz, NH), 2.92 (1 H, d, J_{PH} 9 Hz, NH), and 1.30 (9 H, s) (Found: C, 63.4; H, 7.3; N, 13.8. $C_{16}H_{22}N_3OP$ requires C, 63.35; H, 7.3; N, 13.85%).

Acknowledgements

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