N-(Diphenylphosphinothioyl)hydroxylamine: preparation, characterisation and base-induced transposition of sulfur and oxygen atoms in its *O*-benzoyl derivative[1]

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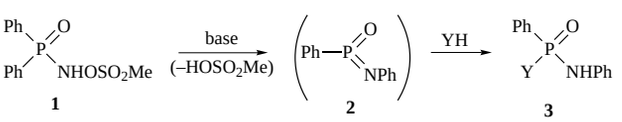
***N*-(Diphenylphosphinothioyl)hydroxylamine 5 has been prepared from $Ph_2P(S)Cl$ using $H_2NOSiMe_3$ and has been converted into its *O*-benzoyl derivative $Ph_2P(S)NHOCOPh$ 6. The principal reaction of the derivative 6 with base (NaOMe or Bu^tNH_2) is rearrangement, transposition of sulfur and oxygen giving $Ph_2P(O)NHSCOPh$ 7; this then reacts further, forming the phosphinic amide $Ph_2P(O)NH_2$ together with $PhCO_2Me$ or $PhCONHBu^t$. The rearrangement probably involves intramolecular nucleophilic displacement of benzoate by the P=S group of 6, forming an intermediate with P, N and S atoms in a three-membered ring.**

Phosphinic chlorides react with hydroxylamine to give *O*-phosphinoylhydroxylamines[2] [$R_2P(O)ONH_2$] and not, as once was thought,[3] the *N*-phosphinoyl compounds. Nonetheless, it is possible, using $H_2NOSiMe_3$ (or $Me_3SiNHOSiMe_3$) in place of H_2NOH, to obtain *N*-phosphinoylhydroxylamines [$R_2P(O)NHOH$] and study their chemistry.[2,4,5] Formally they are phosphorus analogues of hydroxamic acids (RCONHOH),[6] and like them, they form derivatives that rearrange with base. Thus, for example, a phenyl group migrates from phosphorus to nitrogen when the *O*-sulfonyl derivative **1** reacts with methoxide or *tert*-



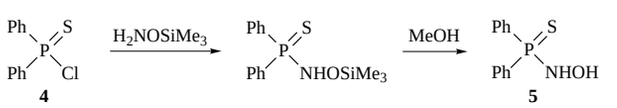
1 **2** **3**

butylamine.[2] The isolated product is a phosphonamidate **3** (Y = MeO) or a phosphonic diamide **3** (Y = Bu^tNH),[2] but the initial product of rearrangement could be a transient metaphosphonimidate **2**, analogous to the isocyanate formed in a Lossen rearrangement.[6] Our concern now is with *N*-thiophosphinoylhydroxylamines [$R_2P(S)NHOH$], a hitherto unknown class of compound, and in particular with the possibility that suitable derivatives might rearrange with base, and that thioxo analogues of **2** might be involved.

Results and discussion

Preparation and characterisation

Thiophosphinoyl compounds are less reactive than their P=O counterparts but the phosphinothioic chloride **4** reacted steadily, over several hours, with $H_2NOSiMe_3$ and Et_3N in CH_2Cl_2 at room temperature. Desilylation of the product gave a crystalline compound having the correct molecular formula for structure **5** (M^+ 249; elemental analysis) and a ^{31}P chemical shift



4 **5**

[$\delta_P(CH_2Cl_2)$ 66.6] indicative of P=S rather than P=O [for $Ph_2P(O)NHOH$, $\delta_P(CHCl_3)$ 28.8]. Apart from the aromatic signals, the ^1H NMR spectrum in $CDCl_3$ contained only a broad 2 H resonance at δ_H 5.2, but in DMSO two distinct phosphorus-coupled signals could be seen, at δ_H 8.28 and 8.04, for the protons of the NHOH group. The *N*-thiophosphinoyl structure **5** seems secure for this compound, which is stable at room temperature and can be stored indefinitely at −20 °C.

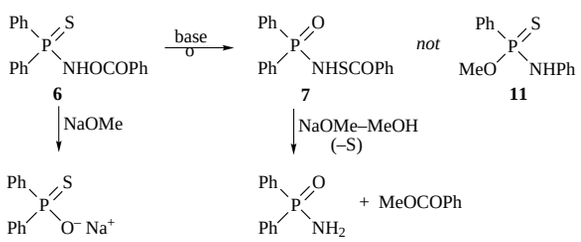
Attempts to make an *O*-sulfonyl derivative of **5**, using tosyl chloride or mesyl chloride with pyridine or Et_3N, invariably ended in failure. The starting material was consumed readily enough (^{31}P NMR spectroscopy) but the reactions were not clean and gave substantial amounts of products having P=O in place of P=S, most notably the amide $Ph_2P(O)NH_2$. It seems probable that sulfonyl derivatives of **5** are formed but are not stable. More success was found with *O*-acyl derivatives, doubtless because carboxylate is a more modest leaving group than sulfonate. With acetic anhydride the product [$Ph_2P(O)NHOAc$; $\nu_{C=O}$ 1755 cm^{-1}, $\delta_P(CH_2Cl_2)$ 65.1] was an oil that could not be thoroughly purified, but with benzoyl chloride a crystalline product was obtained. This had spectroscopic properties in accord with the benzoate structure **6**, in particular $\delta_P(CDCl_3)$ 65.4 (P=S), $\delta_H(CD_3SOCD_3)$ 9.96 (1 H, d, J_{PH} 3) (NH), ν_{max} 1730 cm^{-1} (C=O) and *m/z* 353 (M^+, 20%).

Reaction with methoxide

The benzoate **6** was only slightly soluble in MeOH but when NaOMe (1.2 equiv.; 0.4 mol dm^{-3}) was added it dissolved and reacted over 15 min. Some sulfur was deposited and two phosphorus compounds (δ_P 25.6 and 56.3 in the reaction mixture) were formed in a 10:1 ratio. The major product was isolated and identified as the phosphinic amide **9** (Scheme 1) while the minor product was apparently the phosphinothioate salt **8** since it was converted into the thioester $Ph_2P(O)SMe$ on treatment with MeI. The principal non-phosphorus product (apart from sulfur) was also isolated and was seen to be methyl benzoate **10**. Monitoring the reaction by ^{31}P NMR spectroscopy revealed that only the minor product **8** is formed directly from the substrate **6**; the major product **9** is derived from an intermediate compound having δ_P 31.8. In an attempt to isolate the intermediate the reaction was repeated (at a lower temperature) with quenching (CF_3CO_2H) after just 3 min. The intermediate was the principal component (60%) of the resulting mixture and, by virtue of its low solubility, it could be isolated in a sufficiently pure state for spectroscopic examination. Significant features included $\delta_P(CDCl_3)$ 28.2 (P=O, not P=S); $\delta_H(CDCl_3)$ 5.10 (1 H, d, J_{PH} 10) (P-coupled NH; no other non-aromatic protons); ν_{max} 1685 cm^{-1} (C=O); *m/z* 353 (M^+, 25%) and 105 ($PhCO^+$, 100). The molecular ion is especially revealing; allied with an appreciable M + 2 peak indicative of sulfur (^{34}S), it implies that the intermediate has the same molecular formula as the substrate **6**.

Taken together, the various pieces of structural evidence point to a thiohydroxylamine having Ph_2PO and PhCO groups on the S and/or N atoms. More specifically, the ease with which the benzoyl C=O group is attacked by the methoxide nucleophile, and the presence of a P–N bond in the product **9** derived from the intermediate, suggests the *S*-benzoyl structure **7** rather than the *N*-benzoyl alternative [$PhCONHSP(O)Ph_2$] with the phosphinoyl and benzoyl groups transposed. A decrease of 45 cm^{-1} in $\nu_{C=O}$ in going from substrate to intermediate is not unreasonable for a change from OCOPh to SCOPh.[7]

To establish beyond doubt the identity of the intermediate an authentic sample of the *S*-benzoyl compound **7** was required. The sulfonate **1** is known to be susceptible to nucleophilic attack at the N atom — with Me_2S it forms a sulfilimine salt [$Ph_2P(O)NH\overset{+}{S}Me_2$ $\bar{O}Ms$][8] — so its reaction with thiobenzoate anion ($PhCOS^-$) seemed a possibility. The product was indeed **7** (fully characterised), and this was seen to have exactly the same δ_P and R_f values as the intermediate and essentially the same spectroscopic characteristics. Moreover, it was found to react readily with NaOMe in MeOH, depositing sulfur and forming quantitatively the phosphinic amide **9** and methyl benzoate **10**. It thus seems certain that the substrate **6**, when it reacts with methoxide, initially rearranges to **7**, and that the phosphinic amide product **9** actually emanates from **7** (Scheme 1). The



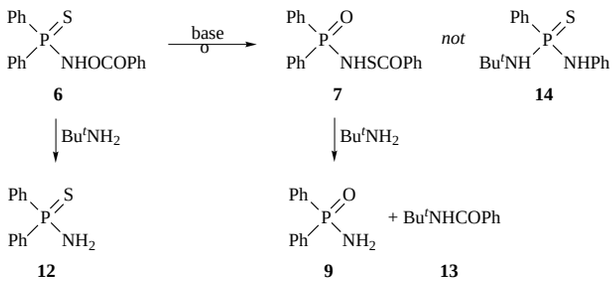
Scheme 1

phosphinothioate product **8** is apparently formed directly from **6**, but this is very much a minor reaction pathway. As regards a Lossen-like rearrangement, comparable with that of the sulfonate **1**, we could find no evidence of the phosphonamidothioate **11** that would be expected as the product. Lacking an authentic sample of **11**, however, it is not possible to rule out the possibility that a small amount was formed but escaped detection.

Reaction with *tert*-butylamine

The reaction of the benzoate **6** with *tert*-butylamine (4 equiv.; 1.5 mol dm^{-3} initial concentration) in CH_2Cl_2 is relatively slow but it too involves an intermediate and two important phosphorus-containing products (Scheme 2). One of the products (δ_P 21.3) is again the phosphinic amide **9**, accompanied now by *N*-*tert*-butylbenzamide **13**, but the other (δ_P 53.7) is the phosphinothioic amide **12** (together, it seems, with $Bu^tNH_3^+$ $\bar{O}COPh$). In the early stages of reaction ($t \leqslant 20$ min; <50% consumption of **6**) the intermediate (δ_P 25.6) is 3–4 times as abundant as either of the products, but it never exceeds 40% of the total reaction mixture, substrate included, and it has not been isolated. However, it has the same R_f as the authentic sample of the *S*-benzoyl compound **7** and the same ^{31}P chemical shift (peak enhanced by addition of **7**). As with methoxide, the intermediate must surely have the structure **7**. It is reasonable to suppose that the phosphinic amide product **9** is formed *via* the intermediate **7** and the phosphinothioic amide **12** directly from the substrate **6** (Scheme 2), and in accord with this is the fact that authentic **7** gives **9** (and $Bu^tNHCOPh$) but not **12** on treatment with *tert*-butylamine. However, the spectra recorded during the reaction of the substrate **6** with *tert*-butylamine suggest that **9** may also be formed by another pathway, not involving **7** as an intermediate.

In contrast to reaction with methoxide, with *tert*-butylamine there was a product (δ_P 60.8), albeit only a very minor one



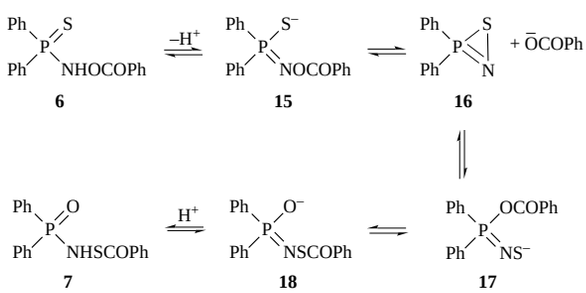
Scheme 2

(~2%), that could conceivably be the Lossen-like rearrangement product **14**. However, an authentic sample of **14**, prepared from the known[9] $PhP(S)(NHBu^t)Cl$ and aniline, was found to have a substantially different chemical shift (δ_P 51.0).

Mechanistic considerations

The apparent unwillingness of the benzoate **6** to undergo Lossen-like rearrangement with base could be accounted for if the thioxo analogue of the intermediate **2** were difficult to form, but that does not seem likely. Three-coordinate P^V species such as **2** are intermediates in other types of reaction, not involving rearrangement,[10] and those that have a P=S group are formed as easily as their P=O counterparts,[11] or in some cases more easily.[12] Rather, it seems likely that something else occurs more readily than phenyl migration when the substrate is a P=S compound.

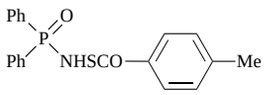
In the Lossen-like rearrangement of the P=O compound **1** the phenyl group that migrates does so as a nucleophile, at least in the sense that electron-donating substituents increase its migratory aptitude while electron-withdrawing substituents reduce it.[13] Sulfur is more nucleophilic than oxygen, at least towards a soft electrophilic centre, so for the P=S compound **6** it could be that intramolecular nucleophilic attack by the S atom is preferred to phenyl migration (Scheme 3). The benzoate



Scheme 3

anion displaced from the N atom of the conjugate base **15** could attack the P atom in **16**, forming **17** and then, by benzoyl transfer, the conjugate base **18** of the phosphinoylthiohydroxylamine intermediate **7**.

If the transformation of **6** into **7** is non-concerted, with a free benzoate anion, a foreign anion $\bar{O}COAr$ should be able to compete with $\bar{O}COPh$ in the formation of **17** (Scheme 3); **7** would then be formed, in part, with COAr on the S atom instead of COPh. To test this, the reaction of the substrate **6** with methoxide was carried out with sodium *p*-toluate (1 equiv.) dissolved in the reaction medium. Unfortunately, in the quenched (CF_3CO_2H) reaction mixture, the ^{31}P NMR signal for **7** was rather broad and the chemical shift for the alternative compound **19** (authentic sample from **1** + $\bar{S}COAr$) was so similar, that it was not possible to tell with confidence if any **19** had



19

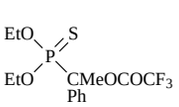
been formed. The experiment was therefore repeated but was now allowed to go to completion. Analysis of the products by GLC showed that $PhCO_2Me$ had been formed, as expected, and that no trace of $ArCO_2Me$ was present. Having confirmed that **19** (authentic sample) does indeed form $ArCO_2Me$ with methoxide, the conclusion is inescapable: benzoate is not liberated during the transformation of **6** into **7**, either because it never becomes completely detached or because the cyclic species **16** (Scheme 3) is so reactive that it recombines with the benzoate anion before it can diffuse away and become free.

As to how the intermediate **7** is converted into the ultimate reaction products, diphenylphosphinic amide **9** and methyl benzoate **10** (Scheme 1) or *N*-*tert*-butylbenzamide **13** (Scheme 2), debenzoylation by nucleophilic attack of methoxide or *tert*-butylamine seems the obvious explanation. Once the benzoyl group has been removed, $Ph_2P(O)NHSH$ might well be unstable, losing sulfur and forming the phosphinic amide.

More puzzling are the products that retain the S atom, *i.e.* phosphinothioate anion **8** with methoxide and phosphinothioic amide **12** with *tert*-butylamine. These are formed directly from the substrate **6**, at least inasmuch as they are not derived from the intermediate **7**. Some other intermediate may be involved, of course, without ever accumulating sufficiently to be detected by ^{31}P NMR spectroscopy. An obvious candidate is the thiophosphinoylhydroxylamine **5** that would result from debenzoylation of the substrate **6**. In a control experiment **5** was seen to react readily with NaOMe in MeOH to give the phosphinothioate **8** (60%) and a small amount of the phosphinic amide **9** (10%) but it also gave a product [$Ph_2P(O)OMe$] having δ_P 34.7 (30%). In the reaction of **6** with methoxide there was no sign of anything with δ_P 30–40, so simple debenzoylation to **5** seems not to be the answer. Even more persuasive is the situation with *tert*-butylamine; the thiophosphinoylhydroxylamine **5** remains totally unchanged (in 1.6 h) under the conditions used for the reaction of **6**. The origin of the sulfur-containing products **8** and **12** remains unclear, and we do not exclude the possibility that a transient species involved in the transformation of **6** into **7**, possibly the cyclic species **16** (Scheme 3), suffers also an alternative fate leading to **8** or **12** rather than **7**.

Conclusion

The *N*-thiophosphinoylhydroxylamine **5** forms an *O*-benzoyl derivative **6** that rearranges with base. This rearrangement is not like that of the phosphinoyl compound **1**, however, since it is the sulfur atom, not a phenyl group, that is transferred from phosphorus to nitrogen. Overall, **6** is transformed into **7** by 1,4-transposition of S and O atoms. There are precedents for 1,3- and 1,5-transpositions of sulfur and oxygen in the chemistry of P=S compounds,[14,15] but more relevant than these is the solvolytic rearrangement of the trifluoroacetate **20**; the product is **22**,



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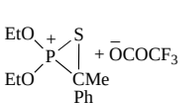

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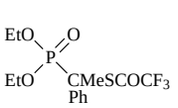

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corresponding to a 1,4-transposition of S and O atoms, and the postulated intermediate **21** is formed by intramolecular nucleophilic displacement of carboxylate by the P=S group in the substrate.[16] The electrophilic centre is carbon, not nitrogen, and no base is needed to bring about reaction, but in other respects there is a marked similarity to our rearrangement of **6** to **7** (Scheme 3).

Experimental

Mps were determined using a Kofler hot-stage apparatus and are uncorrected. ^1H NMR spectra were recorded at 90 MHz on a Varian EM 390 spectrometer (Me_4Si internal standard; coupling constants, *J*, given in Hz) and ^{31}P NMR spectra (^1H decoupled) were recorded at 36.2 MHz on a JEOL JNM-FX90Q spectrometer (positive chemical shifts downfield from external 85% H_3PO_4). Mass spectra were obtained in EI mode on a Kratos Concept spectrometer. GLC analyses were performed using a Philips capillary chromatograph (helium carrier gas, flow rate 16 ml min^{-1}; flame-ionisation detector) fitted with a 15 m × 0.53 mm column containing an immobilised film of SE 54 (1.2 μm) or OV 1701 (1.0 μm) and TLC analyses were performed on silica gel 60 F_{254} (0.2 mm layer on aluminium foil). Methanol was distilled from its magnesium salt and CH_2Cl_2 from CaH_2. Light petroleum refers to the fraction with bp 60–80 °C and ether to diethyl ether.

Diphenylphosphinothioic chloride 4

Chlorodiphenylphosphine (6.62 g, 30.0 mmol) was stirred and heated with sulfur (3.84 g, 120 mmol) in toluene (15 ml) at 105 °C (bath temp.) for 4.5 h. When cold, the mixture was filtered and the solvent evaporated. The crude product was dissolved in ether and the solution was kept at 0 °C overnight to precipitate out remaining sulfur. Distillation afforded diphenylphosphinothioic chloride **4**, bp 180 °C (oven temp.)/0.2 mmHg (lit.,[17] 186–200 °C/1.5 mmHg), $\delta_P(CDCl_3)$ 80.3.

***N*-(Diphenylphosphinothioyl)hydroxylamine 5**

Diphenylphosphinothioic chloride **4** (1.53 g, 6.0 mmol) in CH_2Cl_2 (3 ml) was added to a stirred, ice-cold solution of *O*-(trimethylsilyl)hydroxylamine (0.79 g, 7.5 mmol) and Et_3N (0.61 g, 6.0 mmol) in CH_2Cl_2 (4.5 ml). After 15 min the mixture was allowed to warm to room temperature and stirring was continued overnight. The mixture was then diluted with ether and the precipitate (Et_3NHCl) removed by filtration. The filtrate was concentrated under reduced pressure (no heat) and the residue was dissolved in methanol (3.5 ml). When desilylation was complete (1.5 h; δ_P 65.1→63.7), a half of the solvent was evaporated (taking with it $MeOSiMe_3$) and was replaced by fresh methanol. Addition of water (2 ml) gave *N*-(diphenylphosphinothioyl)hydroxylamine **5** (1.06 g, 71%), mp 114–116 °C; $\delta_P(CH_2Cl_2)$ 66.6; $\delta_H(CDCl_3)$ 8.1–7.7 (4 H, m), 7.5–7.25 (6 H, m) and 5.2 (2 H, broad); $\delta_H(CD_3SOCD_3)$ 8.28 (1 H, d, J_{PH} 7.5), 8.04 (1 H, d, J_{PH} 8.5), 8.0–7.7 (4 H, m) and 7.6–7.4 (6 H, m); ν_{max}(Nujol)/cm^{-1} 3305, 3195, 1120 and 1105; *m*/*z* 249 (M^+, 30%), 233 (30) and 217 (M^+ − NHOH), 100). A sample crystallised from CH_2Cl_2–light petroleum had mp 120–121 °C (Found: C, 57.5; H, 4.5; N, 5.5%; M^+ 249.0378. $C_{12}H_{12}NOPS$ requires C, 57.8; H, 4.85; N, 5.6%; *M* 249.0377).

***N*-(Diphenylphosphinothioyl)-*O*-benzoylhydroxylamine 6**

N-(Diphenylphosphinothioyl)hydroxylamine **5** (315 mg, 1.27 mmol) was dissolved in CH_2Cl_2 (3 ml) with gentle warming. The solution was stirred and cooled in ice and benzoyl chloride (232 mg, 1.65 mmol) was added, followed immediately by Et_3N (132 mg, 1.30 mmol). After 5 min the mixture was allowed to warm to room temperature. It was then diluted with $CHCl_3$ (3 ml), washed with water (2 × 2 ml), dried (Na_2SO_4) and concentrated. Crystallisation from CH_2Cl_2–light petroleum afforded the benzoate **6** (364 mg, 81%), mp 95.5–97 °C; $\delta_P(CDCl_3)$ 65.4; $\delta_H(CDCl_3)$ 8.38 (1 H, s, NH), 8.15–7.7 (6 H, m) and 7.55–7.2 (9 H, m); $\delta_H(CD_3SOCD_3)$ 9.96 (1 H, d, J_{PH} 3, NH) and 8.1–7.4 (15 H, m); ν_{max}(Nujol)/cm^{-1} 3180 (NH) and 1730 (C=O); *m*/*z* 353 (M^+, 20%), 105 ($PhCO^+$, 100) and 77 (35) (Found: C, 64.25; H, 4.4; N, 4.0. $C_{19}H_{16}NO_2PS$ requires C, 64.6; H, 4.6; N, 4.0%).

***N*-(Diphenylphosphinoyl)-*S*-benzoylthiohydroxylamine 7**

A slight excess of thiobenzoic acid (111 mg, 0.80 mmol) was added to a stirred solution of NaOMe (0.75 mmol) in MeOH (3.5 ml), followed by *N*-(diphenylphosphinoyl)-*O*-methylsulfonylhydroxylamine **1** (187 mg, 0.60 mmol).[2] After 1 h the mixture was diluted with water (1 ml), the precipitate was collected, and the crude product (137 mg, 65%) was crystallised

from CH_2Cl_2–light petroleum to give *N*-(diphenylphosphinoyl)-*S*-benzoylthiohydroxylamine **7**, mp 155–156 °C; $\delta_P(CDCl_3)$ 27.9; $\delta_H(CDCl_3)$ 8.15–7.85 (4 H, m), 7.75–7.2 (11 H, m) and 5.0 (1 H, broad); ν_{max}(Nujol)/cm^{-1} 3060 and 2700 (NH), 1685 (C=O) and 1195 (P=O); $\nu_{max}(CH_2Cl_2)$/cm^{-1} 3340 (NH), 1685 (C=O) and 1205 (P=O); *m*/*z* 353 (M^+, 25%), 105 ($PhCO^+$, 100) and 77 (40) (Found: C, 64.3; H, 4.25; N, 3.8. $C_{19}H_{16}NO_2PS$ requires C, 64.6; H, 4.6; N, 4.0%).

N-(Diphenylphosphinoyl)-S-(p-toluoyl)thiohydroxylamine 19

Use of thio-*p*-toluic acid[18] in a preparation similar to that above (but with Bu^tNH_2 as base in place of NaOMe) afforded *N*-(diphenylphosphinoyl)-*S*-(*p*-toluoyl)thiohydroxylamine **19** (92%), crystallised from CH_2Cl_2–ether, mp 163–164 °C; $\delta_P(CDCl_3)$ 27.8; $\delta_H(CDCl_3)$ 8.2–7.85 (4 H, m), 7.55–7.35 (6 H, m), 7.39 (4 H, AA′BB′, δ_A 7.60, δ_B 7.18, J_{AB} 7), 4.9 (1 H, br) and 2.34 (3 H, s); ν_{max}(Nujol)/cm^{-1} 3050 and 2680 (NH), 1690 and 1680 (C=O) and 1190 (P=O); *m*/*z* 367 (M^+, 10%), 119 ($ArCO^+$, 100) and 91 (50) (Found: C, 65.1; H, 4.8; N, 3.7. $C_{20}H_{18}NO_2PS$ requires C, 65.4; H, 4.9; N, 3.8%).

Authentic samples of potential reaction products

Diphenylphosphinic amide **9** was available from other work.[19]

Diphenylphosphinothioic acid was prepared by hydrolysis of diphenylphosphinothioic chloride **4** (2 mol dm^{-3} NaOH, 70 °C, 2 h), mp 139–141 °C (lit.,[20] 141–143 °C), $\delta_P(CDCl_3)$ 75.4; with *tert*-butylamine it formed a salt, $\delta_P(CH_2Cl_2)$ 55.9.

Diphenylphosphinothioic amide **12** was prepared from diphenylphosphinothioic chloride **4** and NH_3 in CH_2Cl_2–MeOH, mp 103–104 °C (from ether–light petroleum) (lit.,[21] 102–104 °C); $\delta_P(CDCl_3)$ 54.9; $\delta_H(CDCl_3)$ 8.1–7.75 (4 H, m), 7.5–7.25 (6 H, m) and 2.85 (2 H, broad s); *m*/*z* 233 (M^+, 70%) and 124 (100); ν_{max}(Nujol)/cm^{-1} 3350 and 3250 (NH_2).

N-*tert*-Butyl-*N*′,*P*-diphenylphosphonothioic diamide **14** was obtained by treating *N*-*tert*-butyl-*P*-phenylphosphonamidothioic chloride[9] with aniline (excess) and Et_3N (1 equiv.) in CH_2Cl_2; after crystallisation from MeOH–H_2O it had mp 125–126 °C; $\delta_P(CDCl_3)$ 51.0 (small impurity, δ_P 51.8); $\delta_H(CDCl_3)$ 8.05–7.75 (2 H, m), 7.5–7.35 (3 H, m), 7.3–6.85 (5 H, m), 5.14 (1 H, d, J_{PH} 8, NH), 2.63 (1 H, d, J_{PH} 9, NH) and 1.36 (9 H, s); ν_{max}(Nujol)/cm^{-1} 3335 and 3320 br (NH); *m*/*z* 304 (M^+, 60%), 212 ($M^+ - NHPh$, 15), 156 ($M^+ - NHPh - C_4H_8$, 100) and 93 (70) (Found: M^+, 304.1164. $C_{16}H_{21}N_2PS$ requires *M*, 304.1163).

N-*tert*-Butylbenzamide **13** was obtained from *tert*-butylamine and benzoyl chloride, mp 137–138 °C (lit.,[22] 134–135 °C); ν_{max}(Nujol)/cm^{-1} 3320 (NH) and 1630 (C=O); $\nu_{max}(CH_2Cl_2)$ 3440 (NH) and 1665 (C=O).

Reactions of N-(diphenylphosphinothioyl)-O-benzoylhydroxylamine 6

(a) Sodium methoxide (0.12 mmol) in MeOH (0.06 ml) was added to a suspension of the substrate **6** (35 mg, 0.10 mmol) in MeOH (0.25 ml). An intense purple colour developed as the substrate dissolved (reacted) over 15 min, being replaced by a yellow colour at the end; δ_P 56.3 (9%) and 25.6 (91%). The solution was neutralised (NH_4Cl) and filtered to remove some sulfur (R_f as for authentic material). Analysis by GLC (SE 54) indicated methyl benzoate **10** (83%) (t_R 2.5 min at 85 °C) and diphenylphosphinic amide **9** (t_R 5.2 min at 190 °C). The solvent was evaporated and the residue was partitioned between CH_2Cl_2 and water. The organic portion was concentrated and the residue was washed with light petroleum. The washing contained methyl benzoate **10** (IR spectrum as for authentic material) and the remaining solid was the phosphinic amide **9**, $\delta_P(CDCl_3)$ 23.1, mp 163–165 °C (from toluene) (lit.,[21] 165–167 °C) (IR and ^{1}H NMR spectra as for authentic material). The aqueous portion was acidified and the liberated acid was extracted into CH_2Cl_2 [δ_P 74.6; $Ph_2P(S)OH$]; it was converted into a salt with Bu^tNH_2 and this was treated with MeI to give *S*-methyl diphenylphosphinothioate, *m*/*z* 248 (M^+, 25%) and 201 (100) (t_R 5.4 min at 190 °C as for authentic material). [A similar experiment using Bu^tNH_3Cl instead of NH_4Cl to neutralise the reaction mixture gave the same results, showing that liberated NH_3 (from NH_4Cl + NaOMe) was not responsible for the formation of the phosphinic amide **9**.]

(b) The reaction of substrate **6** with methoxide was repeated with monitoring by ^{31}P NMR spectroscopy. This revealed an intermediate δ_P 31.8 (*ca.* 50% at *t* = 4 min, 30% at *t* = 6 min) as well as the two products. One of the products (δ_P 25.7) increased as the intermediate declined, the other (δ_P 56.4) did not.

(c) A reaction similar to (a) above was carried out with cooling (*T* ~5 °C) and vigorous shaking; it was quenched by addition of CF_3CO_2H (9 µl) after 3 min (major component, δ_P 29.5, 60%). The solvent was evaporated and the residue was washed with a few drops of MeOH prior to partitioning between $CHCl_3$ and water. The organic portion was concentrated and triturated with ether to give a solid, $\delta_P(CDCl_3)$ 28.2 (impurities 66.2 and 23.4); $\delta_H(CDCl_3)$ 8.1–7.2 (m) and 5.10 (d, J_{PH} 10, NH); mp 144–147 °C; ν_{max}(Nujol)/cm^{-1} 3060 and 2700 (NH), 1685 (C=O) and 1200 (P=O); *m*/*z* 353 (M^+, 25%), 105 (100) and 77 (40); this was apparently (impure) *N*-(diphenylphosphinoyl)-*S*-benzoylthiohydroxylamine **7** (compare authentic material described above).

(d) A reaction similar to (a) above was carried out with sodium *p*-toluate (1 equiv.) dissolved in the reaction mixture. Analysis by GLC (SE 54) showed that methyl benzoate **10** (t_R 2.2 min at 90 °C) had been formed but not methyl *p*-toluate (t_R 4.6 min for an authentic sample) (0.5% would have been detected). As expected, *N*-(diphenylphosphinoyl)-*S*-(*p*-toluoyl)thiohydroxylamine **19** did form methyl *p*-toluate when treated with methoxide.

(e) *tert*-Butylamine (31 mg, 0.43 mmol) was added to the substrate **6** (39 mg, 0.11 mmol) in CH_2Cl_2 (0.25 ml). During 85 min the substrate was converted into an intermediate (δ_P 25.6) and two products, diphenylphosphinic amide **9** (δ_P 21.3) and diphenylphosphinothioic amide **12** (δ_P 53.7). The identities of the products were confirmed by comparison with authentic samples using GLC (SE 54 at 190 °C; t_R 5.0 and 6.0 min for **9** and **12** respectively), TLC and mass spectrometry: **9**, *m*/*z* 217 (M^+, 55%) and 216 (100); **12**, *m*/*z* 233 (M^+, 55%) and 124 (100). The intermediate was identified as the thiohydroxylamine derivative **7** by comparison with the authentic material (^{31}P NMR spectroscopy and TLC).

Two non-phosphorus products were identified, *N*-*tert*-butylbenzamide **13** (43% by GLC), t_R 6.2 min at 110 °C, *m*/*z* 177 (M^+, 20%) and 105 (100), and *tert*-butylammonium benzoate (~40% isolated by precipitation with ether), IR spectrum as for an authentic sample.

Control experiments

(a) *N*-(Diphenylphosphinoyl)-*S*-benzoylthiohydroxylamine **7** reacted with NaOMe (1.5 equiv. as 0.4 mol dm^{-3} solution) in MeOH over 12 min, depositing sulfur and forming diphenylphosphinic amide **9** (δ_P 25.7) as the only phosphorus-containing product [*m*/*z* 217 (M^+, 50), 216 (100) and 199 (60) after isolation; IR spectrum as for authentic sample]. Methyl benzoate **10** [~100% by GLC; t_R 2.5 min (SE 54 at 85 °C)] was also formed.

Compound **7** reacted with Bu^tNH_2 (large excess as 1.5 mol dm^{-3} solution) in CH_2Cl_2 over 0.5 h, forming diphenylphosphinic amide **9** (δ_P 21.8) (70%) and an unidentified product (δ_P 18.4) (30%). The phosphinothioic amide **12** was not formed. *N*-*tert*-Butylbenzamide **13** was also a product (comparison with authentic sample by TLC and GLC).

(b) *N*-(Diphenylphosphinothioyl)hydroxylamine **5** reacted with NaOMe (2.5 equiv. as 0.4 mol dm^{-3} solution) in MeOH to give three substantial products, δ_P 56.4 (50%), 34.7 (30%) and 25.3 (10%), identified as sodium diphenylphosphinothioate **8**, methyl diphenylphosphinate, and diphenylphosphinic amide **9**

respectively by peak-enhancement on addition of the authentic materials; the identities were confirmed by GLC [OV 1701 at 200 °C; t_R 2.0 min for $PhCO_2Me$; 4.5 min for $Ph_2P(O)SMe$ (from **8** with MeI); 7.1 min for **9**].

The hydroxylamine **5** did not react at all with Bu^tNH_2 (large excess as 1.5 mol dm^{-3} solution) in CH_2Cl_2 over 1.6 h (δ_P 63.9 in reaction mixture) and was recovered unchanged (IR spectroscopy).

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