

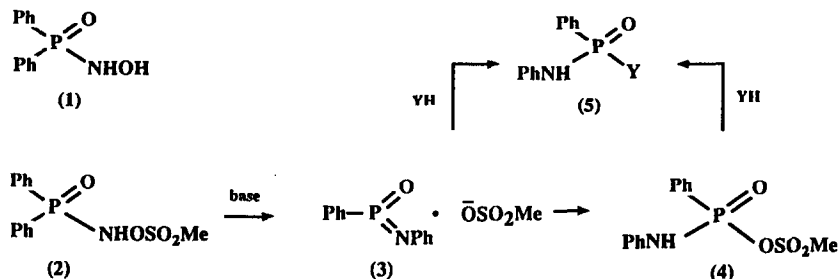
**N,O-BIS(DIPHENYLPHOSPHINOYL) HYDROXYLAMINE
 BASE-INDUCED REARRANGEMENT TO A PHOSPHONAMIDIC-PHOSPHINIC MIXED ANHYDRIDE**

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Summary: The hydroxylamine derivative $Ph_2P(O)NHOP(O)Ph_2$ rearranges on treatment with Bu^tOK-Bu^tOH ; the product contains two dissimilar P atoms (δ_p 24.2 and 7.9, J_{pp} 34 Hz) and is rapidly hydrolysed to a phosphonamidate and a phosphinate, consistent with it being the mixed anhydride $Ph(PhNH)P(O)OP(O)Ph_2$.

N-Phosphinoylhydroxylamines such as (1) form O-sulphonyl derivatives that undergo Lossen-like rearrangements with base.¹ The methanesulphonate (2), for example, is transformed rapidly and cleanly into the phosphonamidic acid derivative (5; Y = OMe) with NaOMe-MeOH and (5; Y = NHBu^t) with Bu^tNH₂. These products could be derived directly from the metaphosponimidate (3). Alternatively, the metaphosponimidate might recombine with the sulphonate anion displaced by the migrating phenyl group, forming a phosphonamidic-sulphonic mixed anhydride (4). Nucleophilic attack at the phosphorus atom in this anhydride would again give the products (5). An anhydride route to product would allow rational explanation of some unexpected features of the rearrangements of (2) and related substrates,² and it is this possibility that has prompted the present investigation.



No direct evidence of a phosphonamidic-sulphonic anhydride was found when the rearrangements of the sulphonyl derivative (2) were monitored by ³¹P n.m.r. spectroscopy. Sulphonate is such a good leaving group, however, that the anhydride may simply not survive long enough to be detected under the conditions required for rearrangement. An alternative derivative of (1) was therefore sought - one that would still undergo rearrangement like the sulphonate, but at the same time would afford a better chance of observing any mixed anhydride that might be formed. An O-phosphinoyl derivative such as (6) seemed particularly attractive, since a phosphonamidic-phosphinic

mixed anhydride should be relatively long-lived and also, with two dissimilar and coupled P atoms, easily recognised by ^{31}P n.m.r. spectroscopy.

The phosphinoylhydroxylamine (1) could not be phosphinylated satisfactorily with diphenylphosphinic chloride, but using *N*-diphenylphosphinoylimidazole, prepared from the phosphinic chloride and *N*-trimethylsilylimidazole, it was smoothly converted into the bisphosphinoyl compound (6) (76%), m.p. 183-184°C (decomp.).³ The ^{31}P n.m.r. spectrum (^1H -decoupled) consisted of a pair of doublets, $\delta_{\text{p}}(\text{CDCl}_3)$ 39.2 and 30.0, J_{pp} 19.5 Hz.⁴

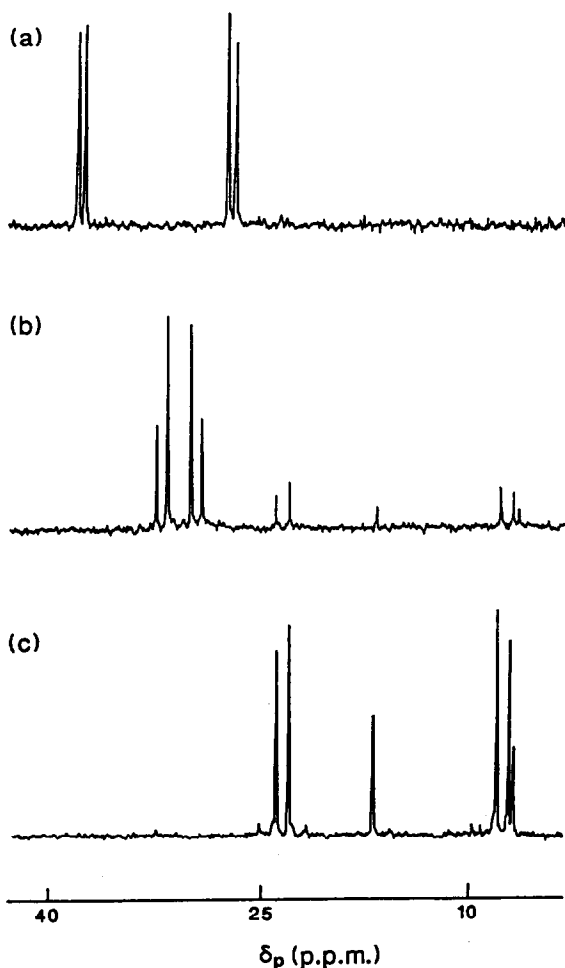
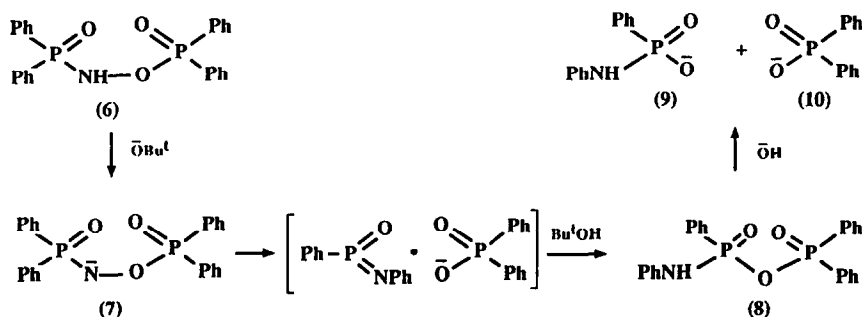


Figure 1. Proton decoupled ^{31}P n.m.r. spectra in $\text{Bu}'\text{OH}$ at 36.2 MHz (2.5 KHz sweepwidth; chemical shifts relative to external 85% H_3PO_4); (a) substrate (6) with no $\text{Bu}'\text{OK}$, (b) with $\text{Bu}'\text{OK}$, $t = 2$ min, (c) with $\text{Bu}'\text{OK}$, $t = 20$ min.

The bis(phosphinoyl)hydroxylamine reacted rapidly with NaOMe-MeOH, but gave no phosphonamidic rearrangement products, only phosphinic degradation products. More interesting were the results obtained with the less nucleophilic Bu^tOK-Bu^tOH. The substrate was only sparingly soluble in Bu^tOH [δ_p 38.8 and 28.1, J_{pp} 20 Hz; Figure 1(a)], but on addition of Bu^tOK (1.5 equiv.) a clear solution was obtained. The ³¹P n.m.r. spectrum, recorded immediately, was seen to be dominated by the 4 lines of an AB pattern, δ_p 32.7 and 30.4, J_{pp} 29 Hz [c.f. Figure 1(b), at $t = 2$ min.]. The dominant species at this stage was apparently the conjugate base (7) of the substrate, since quenching the reaction (CF₃CO₂H) caused unchanged substrate to be precipitated. When left unquenched, the AB pattern was gradually replaced by a new pair of doublets, δ_p 24.2 and 7.9, J_{pp} 34 Hz [Figure 1(c)], together with less intense singlets due to the anions (9) (δ_p 7.0) and (10) (δ_p 17.5),

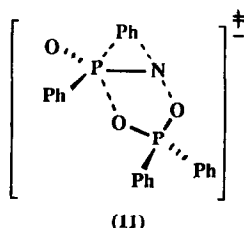


characterised as the methyl ester⁵ and free acid respectively. The compound responsible for the pair of doublets was stable in Bu^tOK-Bu^tOH as long as moisture was excluded, but was rapidly transformed into the anions (9) and (10) by traces of water (hydroxide ion). We think it must be the phosphonamidic-phosphinic mixed anhydride (8), although because of its reactivity we have not been able to isolate it from the rearrangement, or even form it entirely free of its hydrolysis products. We have, however, succeeded in obtaining an essentially pure sample of (8), m.p. 133-135°C, m/z 433 (M^+ , 35%), 341 ($M^+ - NHPH$, 55), and 93 ($PhNH_2^+$, 100), by a different method, namely treatment of the phosphonamidic chloride Ph(PhNH)P(O)Cl with the anion (10) ($Pr^i_2NH_2^+$ cation) under neutral conditions in CH₂Cl₂ solution. The ³¹P n.m.r. spectrum of this material (δ_p 27.2 and 10.4, J_{pp} 34 Hz, in neutral Bu^tOH) is similar to that of the compound formed in the rearrangement, and addition of some of it to the rearrangement reaction mixture produced no new lines in the spectrum. There can be little doubt that the rearrangement does indeed produce the phosphonamidic-phosphinic mixed anhydride.

It is noteworthy that very little (<3%), if any, of the phosphonamidate (5; Y = OBU^t) was formed in the rearrangement. By contrast the corresponding rearrangement of the methanesulphonyl derivative (2) gave (5; Y = OBU^t), m.p. 124°C (decomp.), m/z 289 (M^+ , 8%) and 233 ($M^+ - C_4H_8$, 100), δ_p (Bu^tOH) 10.5, in

practically quantitative yield. This seems to imply that the metaphosponimidate reacts selectively with the phosphinate anion in preference to reaction with the Bu^tOH solvent. Perhaps, in fact, the metaphosponimidate is never fully formed. If when the phenyl group migrates from P to N the departing phosphinate begins to form the new O-P bond before the N-O bond is completely severed, the mixed anhydride will be formed directly, via a transition state such as (11).

Whatever the mechanistic detail, the important point is that the *Q*-phosphinoyl derivative (6) rearranges with base to form a phosphonamidic-phosphinic mixed anhydride. It does not necessarily follow that a phosphonamidic-sulphonic anhydride plays any part in the rearrangement reactions of the *Q*-sulphonyl derivative (2), but the possibility that it does must surely be taken seriously.



References and Footnotes

- M.J.P.Harger, *J.Chem.Soc., Perkin Trans.1*, 1983, 2699;
M.J.P.Harger and A.Smith, *ibid.*, 1985, 1787; 1987, 683.
- e.g. The methanesulphonate (2) reacts with an excess of an equimolar mixture of PrⁱNH₂ and Bu^tNH₂ in CH₂Cl₂ to give the products (5; Y = NHPrⁱ) and (5; Y = NHBu^t) in a ratio that is very sensitive to the concentration of amine:

Total amine concentration	Neat	1.0M	0.2M	0.05M
NHPr ⁱ /NHBu ^t product ratio	1.55	3.6	25	≥100

 Such a large increase in selectivity for the more nucleophilic (less hindered) amine is difficult to understand if the products are derived directly from a metaphosponimidate, but not if they are derived from a phosphonamidic-sulphonic mixed anhydride, provided its behaviour resembles that of a phosphonamidic chloride (S.Freeman and M.J.P.Harger, *J.Chem.Soc., Perkin Trans. 2*, 1988, 81).
- The new compounds (6), (8) (authentic sample), and (3; Y = OBu^t) were fully characterised by spectroscopy and elemental analysis or accurate mass measurement.
- For comparison, the values of δ_p for Ph₂P(O)ONH₂ and Ph₂P(O)NHOH are 38.1 and 29.6 respectively (MeOH solution).
- G.Kh.Kamai, F.M.Kharrasova, and É.A. Érré, *J.Gen.Chem.USSR (Engl.Transl.)*, 1972, 42, 1290; M.J.P.Harger and S.Westlake, *Tetrahedron*, 1982, 38, 1511.