

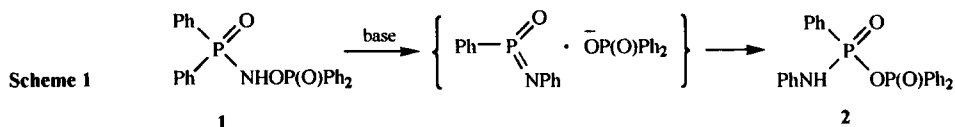
Transposition of the Phosphinoyl Groups in the Base-Induced Rearrangements of *N,O*-Bis(diarylphosphinoyl)hydroxylamines

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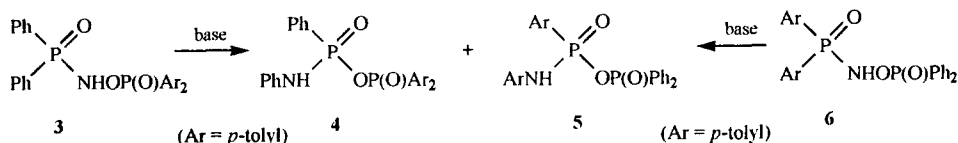
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Abstract: Because the *N*- and *O*-phosphinoyl groups can change places prior to rearrangement, $\text{Ph}_2\text{P}(\text{O})\text{NHOP}(\text{O})\text{Ar}_2$ and $\text{Ar}_2\text{P}(\text{O})\text{NHOP}(\text{O})\text{Ph}_2$ ($\text{Ar} = p\text{-tolyl}$) both give mixtures of two phosphonamidic-phosphinic anhydrides, $\text{Ph}(\text{PhNH})\text{P}(\text{O})\text{OP}(\text{O})\text{Ar}_2$ and $\text{Ar}(\text{ArNH})\text{P}(\text{O})\text{OP}(\text{O})\text{Ph}_2$, on treatment with KOBU^t in Bu^tOH . The transposition of the phosphinoyl groups may involve phosphorane intermediates (7 and 9) having the P atom contained within a three-membered ring
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The bis(phosphinoyl)hydroxylamine **1** is converted into the phosphonamidic-phosphinic mixed anhydride **2** when treated with KOBU^t in Bu^tOH .¹ Presumably the conjugate base of **1** is unstable and rearranges, by fragmentation-recombination with a metaphosphonimidate intermediate (Scheme 1) or by a concerted mechanism. Either way, migration of a phenyl group from P to N transforms the *N*-phosphinoyl moiety of **1** into a phosphonamidoyl group but leaves the *O*-phosphinoyl moiety apparently unchanged. However, when **1** labelled with ^{18}O in the *O*-phosphinoyl moiety is used, the product **2** has some ^{18}O in each of the P=O groups.¹ We have sought clarification of this by looking at the behaviour of two *p*-tolyl analogues of **1**.



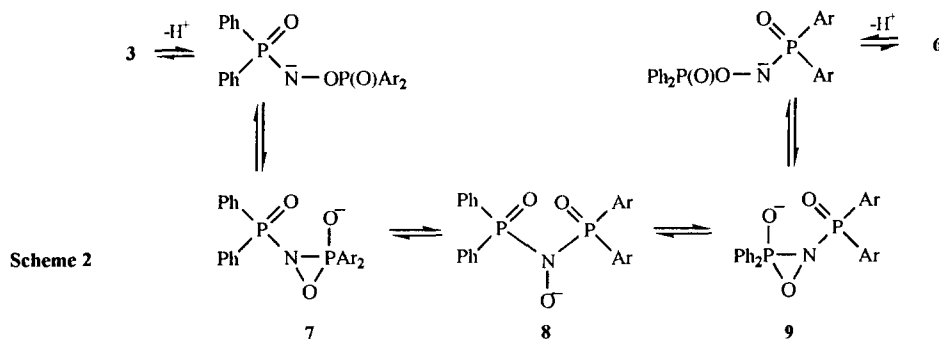
Substrate **3** ($\text{Ar} = p\text{-tolyl}$), m.p. 185-186 °C, δ_{P} (CDCl_3) 29.4 + 40.6 (both d, J_{PP} 19 Hz) was prepared from $\text{Ph}_2\text{P}(\text{O})\text{NHOH}$ with $\text{Ar}_2\text{P}(\text{O})\text{Im}$ ($\text{Im} = \text{imidazo[1-yl]}$) in CH_2Cl_2 .² With KOBU^t (1.5 equiv.) in Bu^tOH (containing 10% C_6D_6 for NMR lock) it gave not one mixed anhydride but two, in a 5:1 ratio: δ_{P} (reaction mixture) 8.4 + 23.6 (major) and 7.3 + 25.0 (minor) (all d, $J_{\text{PP}} \sim 34$ Hz).³ The anhydrides were hydrolysed and the acids esterified (CH_2N_2); the resulting mixture of esters was then analysed by GLC (comparison with authentic samples⁴), GC-MS and ^1H NMR spectroscopy. The minor components, $\text{Ph}(\text{PhNH})\text{P}(\text{O})\text{OME}$ [M^+ 247 (100%)] and $\text{Ar}_2\text{P}(\text{O})\text{OME}$ [M^+ 260 (75%); δ_{H} 2.39 (6 H, s, Me in Ar)], corresponded to the expected product **4**, but the major components, $\text{Ar}(\text{ArNH})\text{P}(\text{O})\text{OME}$ [M^+ 275 (100%); δ_{H} 2.37 and 2.22 (both 3 H, s, Me in Ar)] and $\text{Ph}_2\text{P}(\text{O})\text{OME}$ [M^+ 232 (50%)] were clearly derived from the unexpected mixed anhydride **5**. In confirmation, an authentic sample of the expected anhydride **4** was prepared [$\text{Ph}(\text{PhNH})\text{P}(\text{O})\text{Cl} + \text{OP}(\text{O})\text{Ar}_2$] and was seen to have the same ^{31}P NMR spectrum as the minor product from the rearrangement.



The complementary substrate **6**, m.p. 183–184 °C, δ_{P} (CDCl₃) 30.4 + 39.2 (both d, J_{PP} 19 Hz), was also prepared [Ar₂P(O)NHOH + Ph₂P(O)Im] and treated with KOBu^t. Analysis of the product (³¹P NMR; hydrolysis etc.) again indicated a mixture of the anhydrides **4** and **5**, with the latter again in excess (ratio 1:7). A sample of the major component was isolated and the structure **5** confirmed spectroscopically (¹H NMR; MS).

The reactions of **3** and **6** were repeated but with quenching (CF₃CO₂H) after 2 min. at ca. 25% completion. In both cases the unreacted substrate was seen to be a mixture of **3** and **6** [δ_{P} (Bu^tOH) 27.7 + 39.3 (major) and 28.7 + 38.2 (minor) (all d, J_{PP} 19 Hz)] in a ratio of ca. 2:1.

The implication is clear: a preliminary rearrangement allows the *N*- and *O*-phosphinoyl groups of the substrate to change places (**3** \rightleftharpoons **6**), probably by the mechanism shown in Scheme 2. Here the phosphinoyl groups become equivalent in an intermediate **8** that could be formed *via* a phosphorane **7** or **9** having the P atom contained within a three-membered ring. Equilibration is largely complete before the *N*-phosphinoyl moiety itself



rearranges (P→N migration of Ph or Ar) and favours **3** (as its conjugate base) over **6**, so whichever substrate is used initially an excess of **3** is soon present in the reaction mixture. The major product, however, is not derived from **3**. The less favoured substrate **6** (as its conjugate base) rearranges more quickly, presumably because *p*-tolyl has a higher migratory aptitude than phenyl,⁵ and it is this that gives rise to the major anhydride product **5**.

REFERENCES AND NOTES

- Harger, M.J.P. *Tetrahedron Lett.*, 1990, **31**, 1451 and unpublished observations.
- The new substrates **3** and **6** were fully characterised (NMR, FAB–MS, elemental analysis or accurate M^+).
- The mixed anhydrides **4** and **5** react very rapidly with traces of water in basic media; moisture was excluded as completely as possible but some hydrolysis could not be avoided.
- Harger M.J.P.; Westlake, S. *Tetrahedron*, 1982, **38**, 1511.
- A preference for migration of *p*-tolyl rather than phenyl is seen in the formally-related rearrangement of PhArP(O)NHOSO₂Me (Harger, M.J.P.; Smith, A. *J. Chem. Soc., Perkin Trans. 1*, 1985, 1787).

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