

## Base-induced Rearrangement of the *O*-Methanesulphonyl Derivatives of *N*-(Alkylphenylphosphinoyl)hydroxylamines. Highly Selective Migration of the Phenyl Group

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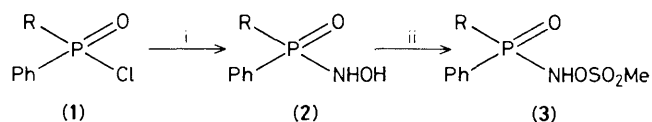
The *N*-(alkylphenylphosphinoyl)-*O*-methanesulphonylhydroxylamines  $RPhP(O)NHOSO_2Me$  ( $R = Me, Et, \text{ or } Pr^i$ ) react readily with  $MeNH_2$  or  $NaOMe-MeOH$  to give products resulting from phenyl, but not alkyl, migration.

*N*-(Diphenylphosphinoyl)hydroxylamine (**2**,  $R = Ph$ ) and some of its derivatives have recently been described.<sup>1</sup> The *O*-methanesulphonate (**3**,  $R = Ph$ ) is of particular interest because of its ready base-induced rearrangement; *e.g.* with  $NaOMe$  in  $MeOH$  it gives the methyl phosphonamidate (**4**).<sup>1</sup> Clearly this transformation involves migration of a phenyl group from phosphorus to nitrogen, but very little is known about the mechanism of the rearrangement or its scope. We have therefore examined some analogues of (**3**,  $R = Ph$ ) which can, in principle, rearrange in two competing ways.

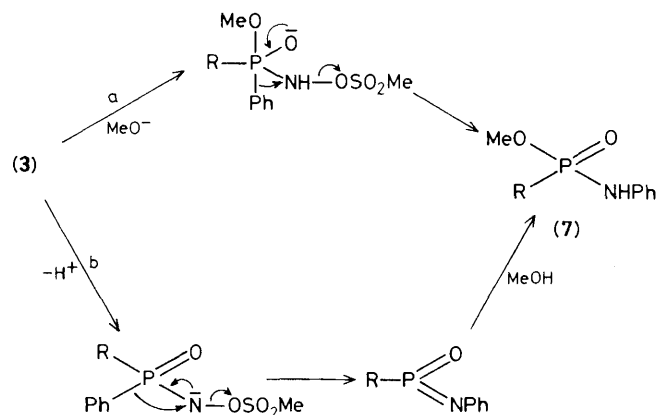
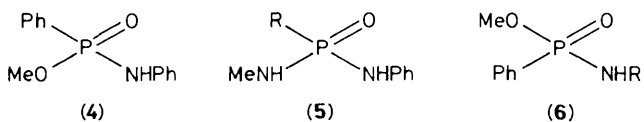
The *N*-(alkylphenylphosphinoyl)hydroxylamines (**2**,  $R = Me, Et, \text{ or } Pr^i$ ) were prepared from the phosphinic chlorides (**1**), and converted into the *O*-methanesulphonyl derivatives (**3**), by methods similar to those developed for the

diphenylphosphinoyl compounds (Scheme 1).<sup>1†</sup> The absence of (**3**,  $R = Bu^t$ ) from our study is a consequence of our inability to prepare (**2**,  $R = Bu^t$ ) because of steric hindrance. The methanesulphonates (**3**) are stable, crystalline compounds characterised by low-field NH doublets ( $\delta$  10.5–10.2,  $J_{PH}$  6–9 Hz) in their <sup>1</sup>H n.m.r. spectra in  $CD_3SOCD_3$ . They reacted vigorously when treated with an excess of anhydrous  $MeNH_2$  ( $T < 0^\circ C$ , no solvent) to give, in each case, a single product ( $\geq 98\%$ ) as indicated by <sup>31</sup>P n.m.r. analysis [ $\delta_P$

† New compounds were fully characterised by spectroscopy and elemental analysis. The compounds (**2**) and (**3**) can be kept at  $-20^\circ C$  for several months without decomposition.



**Scheme 1.** Reagents: i,  $\text{H}_2\text{NOSiMe}_3$ ,  $\text{Et}_3\text{N}$  then  $\text{MeOH}$ ; ii,  $\text{ClOSO}_2\text{Me}$ , pyridine.



**Scheme 2**

( $\text{CH}_2\text{Cl}_2$ ) 25.0, 29.9, and 32.5 for  $\text{R} = \text{Me}$ ,  $\text{Et}$ , and  $\text{Pr}$  respectively].<sup>†</sup> The  $^1\text{H}$  n.m.r. and mass spectra of these products showed them to be the *N*-phenyl-*P*-alkylphosphonic diamides (**5**) resulting from migration of the phenyl group, e.g. for (**5**,  $\text{R} = \text{Me}$ ),  $\delta$  ( $\text{CDCl}_3$ ) 7.35–6.80 (5H, m, NPh), 5.30 (1H, d,  $J_{\text{PH}}$  7 Hz, NH), 2.59 (3H, d,  $J_{\text{PH}}$  12 Hz, NMe), ca. 2.6 br. (NH), and 1.54 (3H, d,  $J_{\text{PH}}$  15 Hz, PMe),  $m/z$  184 ( $\text{M}^+$ , 80%) and 93 ( $\text{PhNH}_2^+$ , 100).

The methanesulphonates (**3**) reacted analogously with  $\text{NaOMe}$  in  $\text{MeOH}$  (2 equiv. of 0.4M solution) to give the

methyl *N*-phenyl-*P*-alkylphosphonamidates (**7**). In this case authentic samples of the alternative (alkyl migration) rearrangement products (**6**) were available,<sup>2</sup> and it was possible to prove conclusively that they were not formed in the rearrangements of (**3**) [ $\leq 1\%$  of (**6**) would have been detected by g.l.c. and/or n.m.r.].<sup>‡</sup>

As well as being an advantage in preparative work, the very high selectivity between potential migrating groups suggests that the methanesulphonates (**3**) do not undergo rearrangement by way of reactive nitrene intermediates. Certainly their behaviour contrasts dramatically with that of the corresponding azides. In the photochemical rearrangement of alkylphenylphosphinic azides,  $\text{RPhP}(\text{O})\text{N}_3$ , in  $\text{MeOH}$  there is little preference for which group migrates, and such discrimination as there is favours alkyl, not phenyl, migration.<sup>2</sup> Two reasonable non-nitrene mechanisms are shown in Scheme 2. To distinguish between them (**3**,  $\text{R} = \text{Me}$ ) and (**3**,  $\text{R} = \text{Pr}$ ) (1 equiv. of each) were mixed and made to compete for  $\text{NaOMe}$  (1 equiv.) in  $\text{MeOH}$ . When the base has been consumed it was seen ( $^{31}\text{P}$  n.m.r.) that ca. 50% of both substrates had been consumed. Equal reactivity is not compatible with path a in Scheme 2; the less hindered substrate (**3**,  $\text{R} = \text{Me}$ ) would be much the more susceptible to nucleophilic attack by methoxide.<sup>3</sup> It is, however, perfectly reasonable for path b, in which the methoxide acts initially as a base and nucleophilic attack at phosphorus occurs only after rearrangement has generated the highly reactive monomeric metaphosphonimide.

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## References

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- 2 M. J. P. Harger and S. Westlake, *Tetrahedron*, 1982, **38**, 3073.
- 3 Many studies have shown the important influence of steric factors on nucleophilic attack at a phosphoryl centre, e.g. A. A. Neimysheva and I. L. Knunyants, *J. Gen. Chem. USSR, (Engl. Transl.)*, 1966, **36**, 1105; M. J. P. Harger, *J. Chem. Soc., Perkin Trans. 1*, 1977, 605.

<sup>‡</sup> In these reactions small amounts of the methyl phosphinates  $\text{RPhP}(\text{O})\text{OMe}$  ( $\text{R} = \text{Me}$ , 10%;  $\text{R} = \text{Et}$ , 1.3%;  $\text{R} = \text{Pr}$ , <1%) were formed.