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

Martin J. P. Harger* and Adrian Smith

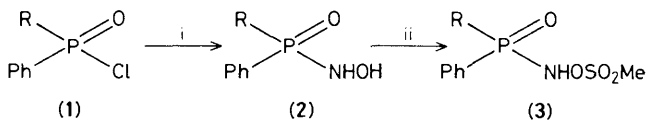
Department of Chemistry, The University, Leicester LE1 7RH, U.K.

The *N*-(alkylphenylphosphinoyl)-*O*-methanesulphonylhydroxylamines RPhP(O)NHOSO$_2$Me (R = Me, Et, or Pr^i) react readily with MeNH$_2$ or NaOMe–MeOH to give products resulting from phenyl, but not alkyl, migration.

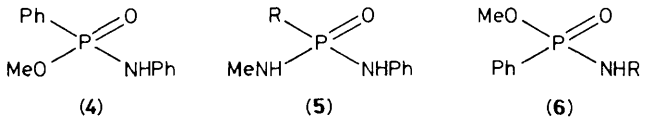
N-(Diphenylphosphinoyl)hydroxylamine (**2**, R = Ph) and some of its derivatives have recently been described.[1] The *O*-methanesulphonate (**3**, R = Ph) is of particular interest because of its ready base-induced rearrangement; *e.g.* with NaOMe in MeOH it gives the methyl phosphonamidate (**4**).[1] 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.

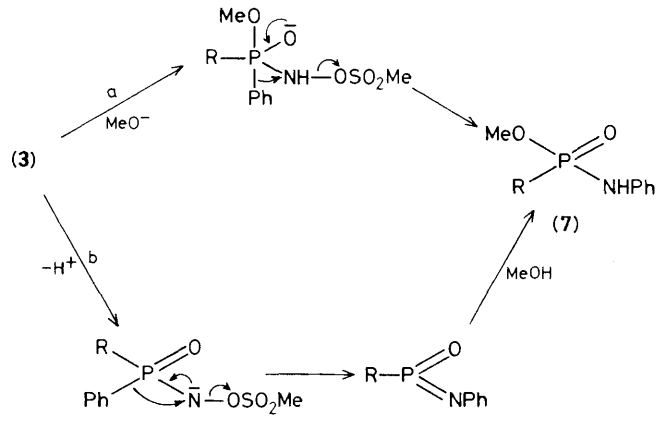
The *N*-(alkylphenylphosphinoyl)hydroxylamines (**2**, R = Me, Et, or Pr^i) were prepared from the phosphinic chlorides (**1**), and converted into the *O*-methanesulphonyl derivatives (**3**), by methods similar to those developed for the diphenylphosphinoyl compounds (Scheme 1).[1†] The absence of (**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 (δ 10.5—10.2, J_{PH} 6—9 Hz) in their ^{1}H n.m.r. spectra in CD_3SOCD_3. They reacted vigorously when treated with an excess of anhydrous MeNH$_2$ ($T < 0$ °C, no solvent) to give, in each case, a single product (≥98%) as indicated by ^{31}P n.m.r. analysis [δ_P

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



Scheme 1. *Reagents:* i, $H_2NOSiMe_3$, Et_3N then MeOH; ii, $ClO-SO_2Me$, pyridine.





Scheme 2

(CH_2Cl_2) 25.0, 29.9, and 32.5 for R = Me, Et, and Pr^i respectively].† The ^{1}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**, R = Me), δ ($CDCl_3$) 7.35—6.80 (5H, m, NPh), 5.30 (1H, d, J_{PH} 7 Hz, NH), 2.59 (3H, d, J_{PH} 12 Hz, NMe), *ca.* 2.6 br. (NH), and 1.54 (3H, d, J_{PH} 15 Hz, PMe), *m/z* 184 (M^+, 80%) and 93 ($PhNH_2^+$, 100).

The methanesulphonates (**3**) reacted analogously with NaOMe in MeOH (2 equiv. of 0.4 M 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,[2] and it was possible to prove conclusively that they were not formed in the rearrangements of (**3**) [≤1% of (**6**) would have been detected by g.l.c. and/or n.m.r.].‡

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, $RPhP(O)N_3$, in MeOH there is little preference for which group migrates, and such discrimination as there is favours alkyl, not phenyl, migration.[2] Two reasonable non-nitrene mechanisms are shown in Scheme 2. To distinguish between them (**3**, R = Me) and (**3**, R = Pr^i) (1 equiv. of each) were mixed and made to compete for NaOMe (1 equiv.) in MeOH. When the base has been consumed it was seen (^{31}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**, R = Me) would be much the more susceptible to nucleophilic attack by methoxide.[3] 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 metaphosphonimidate.

We thank the S.E.R.C. for a research studentship.

Received, 1st June 1984; Com. 765

References

1 M. J. P. Harger, *J. Chem. Soc., Perkin Trans. 1*, 1983, 2699.
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.

‡ In these reactions small amounts of the methyl phosphinates RPhP(O)OMe (R = Me, 10%; R = Et, 1.3%; R = Pr^i, <1%) were formed.