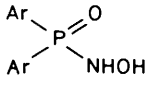
N-[Aryl(phenyl)phosphinoyl]hydroxylamines: Influence of Substituents on the Competitive Migration of Aryl and Phenyl Groups in the Lossen-like Rearrangement of their *O*-Methanesulphonyl Derivatives

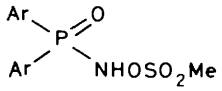
Martin J. P. Harger* and Adrian Smith
Department of Chemistry, The University, Leicester LE1 7RH

The *N*-[aryl(phenyl)phosphinoyl]hydroxylamines ArPhP(O)NHOH (**4**) (Ar = *p*-XC_6H_4; X = MeO, Me, Cl, NO_2) have been prepared from the corresponding phosphinic chlorides (**3**) using *O*-(trimethylsilyl)hydroxylamine and converted into the *O*-methanesulphonyl derivatives (**5**). These rearrange rapidly at 0 °C with NaOMe in MeOH to give the methyl phosphonamidates ArP(O)(OMe)NHPh (**6**) and PhP(O)(OMe)NHAr (**7**). Quantitative analysis of the product mixtures gives the following values for the migration ratio *p*-XC_6H_4/Ph: 30 (X = MeO), 3.3 (X = Me), 0.7 (X = Cl), and 0.065 (X = NO_2).

The first *N*-phosphinoylhydroxylamines (**1**; Ar = Ph, *etc.*) have only recently been described.[1,2] These compounds are the phosphorus analogues of hydroxamic acids (RCONHOH),

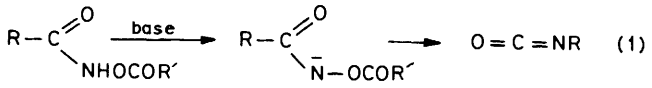


(**1**)



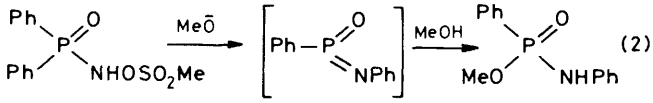
(**2**)

perhaps best known because of the Lossen rearrangement of their *O*-acyl derivatives [equation (1)].[3] No comparable



(1)

reaction has been observed with the *O*-acetyl derivatives of compounds (**1**), but with a leaving group better than acetate rearrangement does occur [equation (2)].[1] In the Lossen



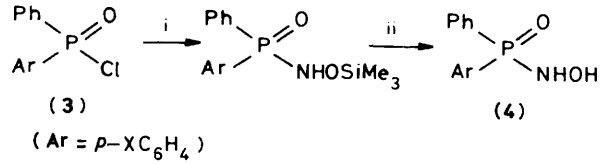
(2)

reaction it is possible to isolate the isocyanate that results from rearrangement,[3,4] but its phosphorus analogue — a monomeric metaphosphonimidate — would dimerise and polymerise in the absence of a suitable trap [*e.g.*, MeOH in equation (2)].[5,6] We have therefore assumed the formation of a metaphosphonimidate,† and have attempted to learn more about the reaction shown in equation (2) by examining how substituents X influence the migration of the phenyl group from P to N. In principle one could compare the rates of rearrangement for a series of compounds (**2**) with Ar = XC_6H_4, but in practice this would be difficult because the reactions are very fast, even at room temperature with a relatively weak base such as t-butylamine in dichloromethane. In any case, since it is presumably the conjugate base of compound (**2**) that actually rearranges, the observed rates (in weakly basic media) would reflect not only the ease of migration of XC_6H_4 but also the influence of X on the acidity of the substrates. We have therefore taken advantage of a consititional feature that distinguishes phosphinoylhydroxylamines from hydroxamic acids, namely the presence in the molecule of two potential migrating groups, and have examined the products of rearrangement of the unsymmetrical compounds (**5**).

† The most plausible alternative to the metaphosphonimidate mechanism involves nucleophilic attack at phosphorus in the substrate. We have recently reported results which seem incompatible with that alternative. See M. J. P. Harger and A. Smith, *J. Chem. Soc., Chem. Commun.*, 1984, 1140.

Results and Discussion

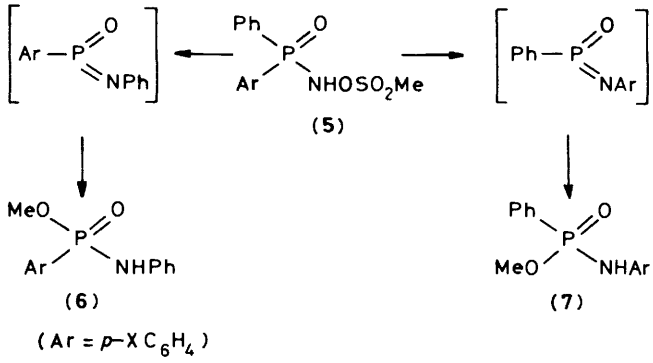
Appropriate *para*-substituted aryl(phenyl)phosphinic acids were prepared from $PhPCl_2$ and *p*-$XC_6H_4N_2BF_4$ (X = MeO, Cl, NO_2) or from $PhP(OEt)_2$ and *p*-XC_6H_4Br (X = Me) by conventional methods, and were converted with thionyl chloride into the phosphinic chlorides (**3**). Reaction with *O*-(trimethylsilyl)hydroxylamine followed by removal of the silyl blocking group then gave the *N*-phosphinoylhydroxylamines (**4**) (Scheme 1). These on treatment with methanesulphonyl



(**3**) (Ar = *p*-XC_6H_4) (**4**)

Scheme 1. *Reagents:* i, $H_2NOSiMe_3$, Et_3N; ii, MeOH (or EtOH)

chloride in pyridine at 0 °C for 6—8 min afforded the *O*-methanesulphonates (**5**), characterised by ^1H n.m.r. spectra [$(CD_3)_2SO$] containing low-field 1 H phosphorus-coupled doublets (J_{PH} 11 Hz, NH) at δ 10.7—11.1 and 3 H singlets (OSO_2Me) at δ 3.25. Both the *N*-phosphinoylhydroxylamines (**4**) and their *O*-methanesulphonates (**5**) decompose at (or below) their m.p., but they were obtained analytically pure by careful crystallisation and could be stored for several months without deterioration at −20 °C. Of the phosphinoylhydroxylamines only (**4**; X = Me) gave a mass spectrum having a



(**5**)

(**6**) (Ar = *p*-XC_6H_4) (**7**)

Scheme 2.

Table. Rearrangement of $ArPhP(O)NHOSO_2Me$ with NaOMe–MeOH at 0 °C. Migration ratio (Ar/Ph) from analysis of products (Ar = p-XC_6H_4)

Substituent in Ar	X = MeO	X = Me	X = Cl	X = NO_2
Ar/Ph by ^1H n.m.r.	~35	3.2	*a*	0.07
Ar/Ph by ^{31}P n.m.r.	30	3.35	0.70	0.055

[a] No suitable signals; g.l.c. ratio 0.66

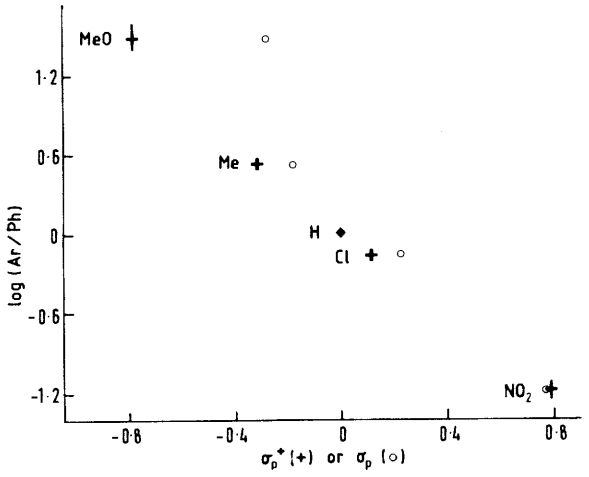
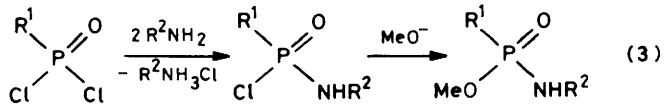


Figure 1. Rearrangement of $ArPhP(O)NHOSO_2Me$ with NaOMe–MeOH at 0 °C. Migration ratio log(Ar/Ph) and values of σ_p^+ (+) and σ_p (○) (Ar = p-XC_6H_4)

significant molecular ion, but all showed conspicuous ($M^+ - 1$) and ($M^+ - 2$) peaks. The methanesulphonates (**5**) all gave reasonably abundant (8—20%) molecular ions and reacted rapidly when suspensions in methanol were treated with sodium methoxide (1.25 mol equiv.) at 0 °C.

In principle the Lossen-like rearrangement of the methanesulphonates (**5**) in methanol can lead to either of the methyl phosphonamidates (**6**) or (**7**) (Scheme 2), depending on which group (Ph or Ar) migrates. Authentic samples of these possible rearrangement products were prepared by the sequence of reactions shown in equation (3) (R^1 = Ph, R^2 = Ar; or R^1 = Ar, R^2 = Ph), except that the p-chlorophenyl compounds were already available from other work.[7] Because the first step in the sequence is not completely selective, the required methyl phosphonamidates were invariably accompanied by small amounts of the corresponding dimethyl phosphonates [$R^1P(O)(OMe)_2$] and phosphonic diamides [$R^1P(O)(NHR^2)_2$]. The diamide impurities were rather difficult to remove, but careful crystallisation, following chromatography in some cases, afforded products of reasonable purity.



With the aid of the authentic methyl phosphonamidates, the products from the reactions of the methanesulphonates (**5**) with NaOMe–MeOH were analysed. In the ^1H n.m.r. spectra (90 MHz; $CDCl_3$ solution) the aromatic signals showed that with X = MeO and X = NO_2 there was one dominant product (>90%), corresponding to migration of Ar and Ph respectively, while with X = Me and X = Cl there were substantial amounts of both possible rearrangement products. For quantitative analysis the P–OMe signals (d, J_{PH} 11 Hz) could be used for X = NO_2 ($\Delta\delta$ 0.10) but in the other cases they were not resolved. For X = Me and X = MeO advantage was taken of the signals from the substituents X. Using ^{31}P n.m.r. spectroscopy (24.3 MHz; MeOH solution) it was possible to obtain completely resolved peaks for the two products (**6**) and (**7**), albeit that the separation was <0.5 p.p.m. with X = Me or X = MeO. G.l.c. (OV 17 or OV 225) also afforded clear separation of compounds (**6**) and (**7**) but because there were signs of decomposition in some cases the results were used only qualitatively. The complete analysis established that compounds (**6**) and (**7**) were the only products formed in significant yield, and that the values of the Ar/Ph migration ratio [corresponding to the (**7**)/(**6**) product ratio] were as shown in the Table. An indication of the uncertainty in the values is given in Figure 1, together with the values of σ^+ and σ for the substituents X.[8]

It is clear from the results in the Table that, relative to the unsubstituted phenyl group, migration is encouraged by electron-releasing substituents and discouraged by electron withdrawal. Considering the nature of the migration terminus, bond formation to the electrophilic N of a singlet nitrene would undoubtedly be assisted by electron-releasing substituents in the migrating group, but the effect would probably be small. Nitrenes generally are highly reactive,[9] and phosphoryl nitrenes especially so, at least in as much as (when generated by azide photolysis) they show exceptionally low selectivity in C–H insertion reactions.[10] Rearrangement of a phosphinoyl nitrene [$ArPhP(O)\ddot{N}$:] is likely to be an exothermic process with a small activation energy and an early transition state. In such a transition state there would be little development of the bond from the migrating group to the migration terminus and in consequence probably rather little discrimination (on electronic grounds) between competing migrating groups. The selectivity observed in our experiments is greater than we would expect for a nitrene rearrangement. Certainly it exceeds that associated with the thermolysis of aryldiphenylmethyl azides ($ArPh_2CN_3$).[11] There the (statistically corrected) migratory aptitude relative to Ph is only 2.5 for p-$MeOC_6H_4$, and 0.2 for p-$NO_2C_6H_4$, and even then it is doubtful if the nitrene is fully developed before the migrating group begins to bond to N.[11]

The alternative to a nitrene intermediate is a concerted mechanism, with the developing $\delta+$ charge created by the departing leaving group being accommodated largely by the migrating aryl group (Figure 2). A mechanism of this kind is now generally accepted for the Lossen rearrangement of hydroxamic acid derivatives.[12,*] Although limited in scope, our

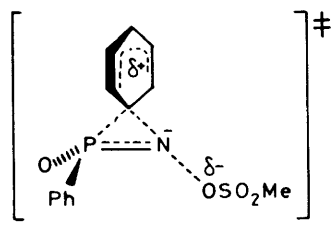
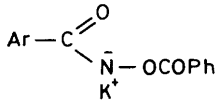


Figure 2.

* A dependence of the Ar/Ph migration ratio on the nature of the leaving group would provide convincing evidence for concertedness in the rearrangement of PhArP(O)NHZ (Z = OSO_2Me, *etc.*). Unfortunately, rearrangement does not occur with Z = OAc and our attempts to introduce other leaving groups [*e.g.*, Z = $OCOCF_3$, $OP(O)Ph_2$] have been largely unsuccessful. We have been able to prepare the *O*-*p*-nitrobenzenesulphonate of (**4**; X = Me) [m.p. 124—125 °C (decomp.); Found: C, 52.5; H, 3.9; N, 6.5. $C_{19}H_{17}N_2O_6PS$ requires C, 52.8; H, 4.0; N, 6.5%], but here the leaving group differs little from methanesulphonate [D. A. Noyce and J. A. Virgilio, *J. Org. Chem.*, 1972, **37**, 2643] and, not surprisingly, it gave the products (**6**) and (**7**) (X = Me) in the same ratio (within experimental error) as did the *O*-methanesulphonate.

results show that the effects of substituents in the aryl group correlate much better with σ^+ ($\rho \sim -1.7$) than with σ (Figure 1). Two features are particularly noteworthy: the *p*-$MeOC_6H_4$/Ph ratio is an order of magnitude greater than the *p*-MeC_6H_4/Ph ratio, and the *p*-ClC_6H_4/Ph ratio is close to unity. Taken together these strongly suggest that the π system of the migrating aryl group is heavily involved in making the new bond to N, *i.e.* the transition state has the aryl group orientated so that its *p* orbitals are parallel to the P–N bond (Figure 2).

In a normal Lossen rearrangement there is only one group that can migrate and so direct comparison of different groups is not possible. However, an indication of migratory aptitudes can be obtained from the kinetic work of Bright and Hauser.[13] For



(8)

the salts (**8**; Ar = *p*-XC_6H_4) they found that the relative rates of rearrangement in 0.1M-aqueous NH_3 were as follows:

X in Ar	MeO	Me	H	Cl	NO_2
$k_{rel.}$	6.8	2.6	1.0	0.3	0.014

In detail these substituent effects differ considerably from ours, and correlate with σ rather than σ^+,[14] but at least the variations are of comparable magnitude. Differences in detail are hardly surprising, bearing in mind that the C atom of a carbonyl group is trigonal and can form 2*p*—2*p* π bonds, whereas the P atom of phosphoryl group is tetrahedral and must use 3*d* orbitals in π bonds.

The ratio of the products from the rearrangement of an unsymmetrical substrate (**5**) will obviously depend on the relative ability of the two potential migrating groups to accommodate the charge (δ+) in the rearrangement transition state. Less obviously, it will also depend to some extent on their relative fitness to stay at the migration origin and become the *P*-aryl group in the monomeric metaphosphonimidate. In common with monomeric metaphosphate, metaphosphonimidates contain quinquevalent trico-ordinate phosphorus.[5] They will be powerful electrophiles and should be stabilised by electron-releasing *P*-aryl groups. The electronic effects of substituents at a phosphoryl centre are generally rather small,[15,16] but could be quite significant when the phosphorus is 3-co-ordinate and highly electrophilic. Any product character in the rearrangement transition state will then encourage the phosphorus to retain the more electron-releasing aryl group, so the group that is the better equipped to migrate is also the one more suited to remain at phosphorus. Thus there will be a levelling effect, with the observed product ratios understating the importance of charge accommodation by the migrating group in the transition state. How significant the levelling effect is we cannot say since we have no information on the relative abilities of the different aryl groups to stabilise the P atom in a metaphosphonimidate.

Experimental

M.p.s were determined using a Kofler hot-stage apparatus. I.r. spectra were recorded with a Perkin-Elmer 298 instrument, and ^1H n.m.r. spectra with a Varian EM390 spectrometer except that ^{31}P-decoupled spectra were obtained using a Varian T-60 instrument coupled to an NMR Specialities HD 60 heteronuclear decoupler. ^{31}P N.m.r. spectra (^1H-decoupled) were recorded at 24.3 MHz with a JEOL JNM-FX60 spectrometer; positive chemical shifts are downfield from external 85% H_3PO_4. Mass spectra were obtained with a V.G. Micromass 16B instrument. G.l.c. analyses were performed on a Pye 104 flame-ionisation chromatograph (on-column injection) fitted with 1.5 m × 4 mm internal diameter glass columns packed with the stated stationary phase coated on silanised 100—120 mesh diatomite C 'Q'. Methanol was purified by distillation from its magnesium salt, and ethyl acetate by distillation from P_2O_5.[17] Copper(I) bromide[18] and nickel(II) bromide were thoroughly dried *in vacuo* before use. *O*-(Trimethylsilyl)hydroxylamine was prepared as previously described.[1] Dichloro(phenyl)phosphine and phenylphosphonic dichloride were commercial materials. Phosphinoylhydroxylamines and their sulphonyl derivatives were stored at −20 °C.

Aryl(phenyl)phosphinic Acids.—These preparations were based on literature methods. (*a*) Dichloro(phenyl)phosphine was allowed to react with *p*-methoxy-[19] or *p*-chloro-benzenediazonium fluoroborate[20] in ethyl acetate containing anhydrous copper(I) bromide. Water was added to hydrolyse the intermediate and then an additional similar volume of water was added; *p*-methoxyphenyl(phenyl)phosphinic acid (60%), m.p. 182—183 °C (lit.,[19] 184 °C) or *p*-chlorophenyl(phenyl)-phosphinic acid (51%), m.p. 152—154 °C (lit.,[20] 154—156 °C) slowly crystallised out.

(*b*) A similar reaction using *p*-nitrobenzenediazonium fluoroborate was carried out as described by Freedman and Doak,[21] except that after the steam distillation there remained an upper liquid layer and a lower semi-solid layer. The upper layer was removed and cooled in ice, when solid deposited. The lower layer was dissolved in aqueous NaOH and the solution was washed with ether and then acidified to give more solid. The combined solids were crystallised from ethyl acetate to give *p*-nitrophenyl(phenyl)phosphinic acid (24%), m.p. 150 °C (lit.,[21] 153—154 °C).

(*c*) Using the method of Tavs,[22] ethyl phenyl(*p*-tolyl)-phosphinate (b.p. 168—174 °C at 0.7 mmHg) was prepared by heating an equimolar mixture of diethyl phenylphosphonite* and *p*-bromotoluene with anhydrous nickel(II) bromide (0.1 mol equiv.) at 160 °C (very vigorous after 45 min induction period). The phosphinate was hydrolysed by being boiled with 10M-aqueous HCl for 9 h to give, after crystallisation from aqueous ethanol, phenyl(*p*-tolyl)phosphinic acid (41%), m.p. 133—135 °C (lit.,[23] 134—136 °C).

Aryl(phenyl)phosphinic Chlorides (**3**).—The phosphinic acids and thionyl chloride (3—4 mol equiv.) were boiled under reflux for 2 h and the products were isolated by kugelrohr distallation. This gave the following chlorides:

(**3**; X = MeO),[24] b.p. 200 °C (oven temp.) at 0.5 mmHg.

(**3**; X = Me), b.p. 160 °C (oven temp.) at 0.2 mmHg (lit.,[25] 163—167 °C at 0.4 mmHg).

(**3**; X = Cl), b.p. 155 °C (oven temp.) at 0.2 mmHg (lit.[25] 155—157 °C at 0.3 mmHg).

(**3**; X = NO_2),[26] b.p. 200 °C (oven temp.) at 0.01 mmHg.

N-[*Aryl(phenyl)phosphinoyl*]*hydroxylamines* (**4**).—In a typical preparation, a solution of *p*-tolyl(phenyl)phosphinic chloride (**3**; X = Me) (1.95 g, 7.8 mmol) in dichloromethane (4 ml) was added during 15 min to a stirred solution of *O*-(trimethylsilyl)hydroxylamine (1.0 g, 9.5 mmol) and triethylamine (1.0 g, 10 mmol) in dichloromethane (10 ml) at 0 °C. The mixture was stirred at 0 °C for a further 2.5 h, then ether (30 ml) was added and the precipitated Et_3NHCl was removed by filtration. Volatile material was evaporated under reduced

* *Cf.* O. Korpiun, R. A. Lewis, J. Chikos, and K. Mislow, *J. Am. Chem. Soc.*, 1968, **90**, 4842 for dimethyl phenylphosphonite.

pressure (gentle warming only) and the residue was desilylated by being stirred with methanol (1 ml) and triethylamine (1 ml) at 0 °C for 8 min.* Ice and water (*ca.* 30 ml total) were then gradually added until a solid precipitated. This was collected by filtration and dried thoroughly over P_2O_5 at *ca.* 0.1 mmHg to give N-[p-*tolyl(phenyl)phosphinoyl*]*hydroxylamine* (**4**; X = Me) (1.27 g, 66%), m.p. 122—123 °C (decomp.); *m/z* 247 (M^+, 25%), 246 (20), and 245 (20); $\nu_{max.}$(Nujol) 3 240, 3 190 (NHOH), and 1 170 cm^{-1} (P=O); δ[$(CD_3)_2SO$] 8.2—8.0 (2 H; includes δ 8.11, d, J_{PH} 11 Hz), 7.85—7.3 (7H; includes δ 7.65, dd, J_{PH} 12, J_{HH} 9 Hz), 7.24 (2 H, dd, J_{PH} 3, J_{HH} 9 Hz), and 2.32 (3 H, s). An analytical sample, crystallised from aqueous methanol, had m.p. 118—120 °C (decomp.) (Found: C, 63.2; H, 5.7; N, 5.4. $C_{13}H_{14}NO_2P$ requires C, 63.15; H, 5.7; N, 5.7%).

N-[p-*Chlorophenyl(phenyl)phosphinoyl*]*hydroxylamine* (**4**; X = Cl) was similarly prepared (reaction time 4.5 h at 0 °C), desilylation being achieved with ethanol (1.5 ml) and triethylamine (0.8 ml) at 0 °C overnight.* The product (67%) after crystallisation from aqueous methanol had m.p. 119—120 °C (decomp.), *m/z* 268, 266 (M^+ − 1, 12%)and 267, 265 (12) (M^+ not observed); $\nu_{max.}$(Nujol) 3 270, 3 195 (NHOH), 1 190, and 1 185 cm^{-1} (P=O); δ[$(CD_3)_2SO$] 8.4—8.15 (2 H; includes δ 8.30, d, J_{PH} 13 Hz) and 7.9—7.25 (9 H) (Found: C, 54.1; H, 4.4; N, 5.3. $C_{12}H_{11}ClNO_2P$ requires C, 53.85; H, 4.15; N, 5.2%).

N-[p-*Methoxyphenyl(phenyl)phosphinoyl*]*hydroxylamine* (**4**; X = MeO) was similarly prepared (reaction time 1.5 h at room temperature), desilylation being achieved with methanol (2 ml) and triethylamine (0.5 ml) at 0 °C for 10 min.* On addition of ice–water the product (61%) separated as a thick oil which solidified as the mixture was stirred. After crystallisation from aqueous methanol the product had m.p. 119—121 °C (decomp.), *m/z* 262 (M^+ − 1, 100%) and 261 (90) (M^+ not observed); $\nu_{max.}$(Nujol) 3 300—3 000br (NHOH), 1 185, and 1 170 cm^{-1} (P=O); δ[$(CD_3)_2SO$] 8.2—8.0 (2 H; includes δ 8.10, d, J_{PH} 12 Hz), 7.85—7.3 (7 H; includes δ 7.67, dd, J_{PH} 11, J_{HH} 9 Hz), 6.98 (2 H, dd, J_{PH} 3, J_{HH} 9 Hz), and 3.76 (3 H, s) (Found: C, 59.6; H, 5.4; N, 5.3. $C_{13}H_{14}NO_3P$ requires C, 59.3; H, 5.4; N, 5.3%).

N-[p-*Nitrophenyl(phenyl)phosphinoyl*]*hydroxylamine* (**4**; X = NO_2) was similarly prepared (reaction time 2.8 h at 0 °C) except that after filtration and evaporation of volatile material the silylated phosphinoylhydroxylamine was isolated by addition of water, and the resulting solid was dried. Desilylation was achieved by dissolution of the solid in dichloromethane (40 ml) containing methanol (1.8 ml). After 3 h at room temperature volatile material was removed under reduced pressure (gentle warming) and fresh dichloromethane (5 ml) was added to the residue. The product (**4**; X = NO_2) (38%) crystallised out slowly at 0 °C, m.p. 105—107 °C (decomp.); *m/z* 277 (M^+ − 1, 95%) and 276 (100) (M^+ not observed); $\nu_{max.}$(Nujol) 3 300, 3 150br (NHOH), 1 520, 1 350 (NO_2), 1 200, and 1 190 cm^{-1} (P=O); δ[$(CD_3)_2SO$] 8.65—7.3 (complex). Analytically pure material crystallised from aqueous methanol, m.p. 113—115 °C (decomp.) (Found: C, 51.8; H, 4.0; N, 9.9. $C_{12}H_{11}N_2O_4P$ requires C, 51.8; H, 4.0; N, 10.1%).

N-[*Aryl(phenyl)phosphinoyl*]-O-*methylsulphonylhydroxylamines* (**5**).—The *N*-phosphinoylhydroxylamine (0.5 g) was mixed well with pyridine (*ca.* 1.5 ml) at 0 °C and methanesulphonyl chloride (*ca.* 1.3 mol equiv.) was added. The mixture was shaken and cooled for 8 min and then immediately quenched with ice–water (10—20 ml). The product usually separated as a solid or an oil that soon solidified. When an oil persisted the water was decanted off, the residue was triturated with a few drops of methanol until a solid formed, and fresh ice–water was added. The solid was filtered off, washed thoroughly with water, dried over P_2O_5 at *ca.* 0.1 mmHg, and crystallised from methanol (brief heating). The following methanesulphonates were obtained:

(**5**; X = MeO) (53%), m.p. 126.5—128.5 °C (decomp.); *m/z* 341 (M^+, 20%); $\nu_{max.}$(Nujol) 3 140 (NH), 1 200, and 1 180 cm^{-1} (P=O); δ[$(CD_3)_2SO$] 10.76 (1 H, d, J_{PH} 11 Hz), 7.9—7.4 (7 H; includes δ 7.71, dd, J_{PH} 12, J_{HH} 9 Hz), 7.08 (2 H, dd, J_{PH} 3, J_{HH} 9 Hz), 3.79 (3 H, s), and 3.24 (3 H, s); δ_P(MeOH) 31.3 p.p.m. (Found: C, 49.3; H, 4.75; N, 4.0. $C_{14}H_{16}NO_5PS$ requires C, 49.3; H, 4.7; N, 4.1%) (in this case the reaction time was reduced to 6 min).

(**5**; X = Me) (63%), m.p. 151—152 °C (decomp.); *m/z* 325 (M^+, 20%); $\nu_{max.}$(Nujol) 3 135 (NH), 1 200, and 1 180 cm^{-1} (P=O); δ[$(CD_3)_2SO$] 10.95 (1 H, d, J_{PH} 11 Hz), 7.9—7.45 (7 H; includes δ 7.68, dd, J_{PH} 12, J_{HH} 8 Hz), 7.37 (2 H, dd, J_{PH} 3, J_{HH} 8 Hz), 3.24 (3 H, s), and 2.36 (3 H, s); δ_P(MeOH) 31.2 p.p.m. (Found: C, 51.6; H, 4.9; N, 4.4. $C_{14}H_{16}NO_4PS$ requires C, 51.7; H, 5.0; N, 4.3%).

(**5**; X = Cl) (56%), m.p. 137—139 °C (decomp.); *m/z* 347 and 345 (ratio 1:3, M^+, 15%); $\nu_{max.}$(Nujol) 3 140 (NH), 1 205, and 1 180 cm^{-1} (P=O); δ[$(CD_3)_2SO$] 10.92 (1 H, d, J_{PH} 11 Hz), 7.95—7.45 (9 H, m), and 3.25 (3 H, s); δ_P(MeOH) 29.7 p.p.m. (Found: C, 45.2; H, 3.8; N, 4.2. $C_{13}H_{13}ClNO_4PS$ requires C, 45.2; H, 3.8; N, 4.05%).

(**5**; X = NO_2) (78%), m.p. 146—147 °C (decomp.); *m/z* 356 (M^+, 8%); $\nu_{max.}$(Nujol) *ca.* 3 000 (shoulder on Nujol), 2 800 (NH), 1 210, and 1 190 cm^{-1} (P=O); δ[$(CD_3)_2SO$] 11.09 (1 H, d, J_{PH} 11 Hz), 8.37 (2 H, dd, J_{PH} 2, J_{HH} 9 Hz), 8.25—7.4 (7 H, m), and 3.26 (s; integration precluded by proximity of peak due to H_2O in solvent); δ_P(MeOH) 27.9 p.p.m. An analytical sample had m.p. 138—139 °C (decomp.) (Found: C, 43.8; H, 3.7; N, 7.9. $C_{13}H_{13}N_2O_6PS$ requires C, 43.8; H, 3.7; N, 7.9%). (For this preparation the quantity of pyridine was reduced to 0.7 ml.)

Reactions of N-[*Aryl(phenyl)phosphinoyl*]-O-*methylsulphonylhydroxylamines* (**5**) *with Methanolic Sodium Methoxide.*—A suspension of the substrate (**5**) (0.12 mmol) in methanol (1.1 ml) was cooled in ice and 2M methanolic sodium methoxide (0.15 mmol) was added. A clear solution was obtained almost immediately but the reaction mixture was left for 10 min before ammonium chloride (0.1 mmol) was added to neutralise the excess of methoxide, and the ^{31}P n.m.r. spectrum was recorded. The solvent was then removed under reduced pressure and chloroform (6 ml) and water (1 ml) were added to the residue. The organic layer was separated, dried (Na_2SO_4), and evaporated to dryness. The product was then examined by g.l.c., and ^1H n.m.r. (in $CDCl_3$) and ^{31}P n.m.r. spectroscopy (in MeOH) to determine the ratio (**7**)/(**6**); the characteristics of the compounds are detailed for the authentic samples (see below).† The identities of g.l.c. and ^{31}P n.m.r. peaks were confirmed by enhancement on addition of authentic material. (The water layer from the work-up was examined by ^{31}P n.m.r. spectroscopy to ensure that nothing of significance had been removed).

Authentic Samples of Rearrangement Products (**6**) *and* (**7**).—Diethyl *p*-methoxyphenyl-[27] and *p*-tolyl-phosphonate[22] were converted into the corresponding phosphonic dichlorides[28] by the addition of PCl_5 (no solvent) and then heating under reflux overnight.[28] *p*-Nitrophenylphosphonic acid[29] was converted

* Triethylamine was present during the desilylation to minimise the risk of acid-catalysed P–N bond cleavage. In view of the recent observation of base-induced decomposition of $Ph_2P(O)NHOH$ (ref. 2) this may have been unwise.

† Chemical shifts in the ^1H n.m.r. spectra of the product mixtures generally differed somewhat from those of the separate compounds, *e.g.*, the P–OMe signal of (**7**; X = NO_2) appeared ~0.1 p.p.m. upfield in the product mixture obtained from (**5**; X = NO_2).

into the dichloride[30] by dissolution in an excess of $SOCl_2$ and boiling under reflux for 5 h. The arylphosphonic dichlorides were isolated by vacuum kugelrohr distillation, and were then treated as follows.

A solution of the phosphonic dichloride in dichloromethane (or ether) was stirred at 0 °C while a solution of the aromatic amine (2 mol equiv.) dissolved in the same solvent was gradually added. The mixture was stirred at room temperature until no more amine hydrochloride precipitated. Exceptionally for (**7**; X = NO_2), solid *p*-nitroaniline (1 mol equiv.) was added in several portions to a mixture of phenylphosphonic dichloride (1 mol equiv.) and Et_3N (1 mol equiv.) in dichloromethane and (because the reaction was exceptionally slow) the mixture was stirred overnight. The amine hydrochloride was removed by filtration and the filtrate was stirred while a solution of sodium methoxide (2 mol equiv.) in methanol was added. Volatile material was evaporated off and the residue, dissolved in dichloromethane, was washed with water. After evaporation of the solvent, the product was purified by crystallisation [after chromatography on alumina for (**6**; X = MeO) and (**7**; X = NO_2)] but was often still contaminated with a small amount of the phosphonic diamide. The following were prepared: (**6**; X = MeO), m.p. 109—111 °C; *m/z* 277 (M^+, 85%) and 185 (M^+ − NHPh, 100); δ($CDCl_3$) 7.71 (2 H, dd, J_{PH} 13, J_{HH} 9 Hz), 7.2—6.7 (8 H, m, includes NH), 3.76 (3 H, d, J_{PH} 11 Hz), and 3.72 (3 H, s); δ_P(MeOH) 21.13 p.p.m. (Found: M^+, 277.0865. $C_{14}H_{16}NO_3P$ requires *M*, 277.0868).

(**7**; X = MeO), m.p. 125—127 °C (lit.,[31] 125—127 °C); *m/z* 277 (M^+, 95%) and 155 (M^+ − NHAr, 100); δ($CDCl_3$) 7.9—7.2 (5 H, m), 6.9—6.6 (4 H, AA′ BB′ pattern centred at δ 6.75), 6.52 (1 H, d, J_{PH} 6 Hz), 3.78 (3 H, d, J_{PH} 11 Hz), and 3.65 (3 H, s); δ_P(MeOH) 20.72 p.p.m.

(**6**; X = Me), m.p. 111—112 °C (lit.,[32] 65 °C); *m/z* 261 (M^+, 100%) and 169 (M^+ − NHPh, 80); δ($CDCl_3$) 7.65 (2 H, dd, J_{PH} 14, J_{HH} 9 Hz), 7.3—6.75 (7 H, m), 6.31 (1 H, d, J_{PH} 6 Hz), 3.77 (3 H, d, J_{PH} 11 Hz), and 2.32 (3 H, s); δ_P(MeOH) 20.92 p.p.m.

(**7**; X = Me), m.p. 121—123 °C (lit.,[31] 124—125 °C); *m/z* 261 (M^+, 100%) and 155 (M^+ − NHAr, 40); δ($CDCl_3$) 7.95—7.2 (5 H, m), 7.0—6.7 (4 H, m), 6.00 (1 H, d, J_{PH} 6 Hz), 3.77 (3 H, d, J_{PH} 11 Hz), and 2.17 (3 H, s); δ_P(MeOH) 20.47 p.p.m.

(**6**; X = NO_2), m.p. 113—115 °C; *m/z* 292 (M^+, 100%) and 200 (M^+ − NHPh, 16); δ($CDCl_3$) 8.25—7.8 (4 H, m), 7.2—6.8 (5 H, m), 6.70 (1 H, d, J_{PH} 7 Hz), and 3.85 (3 H, d, J_{PH} 11 Hz); δ_P(MeOH) 16.60 p.p.m. (Found: M^+, 292.0607. $C_{13}H_{13}N_2O_4P$ requires *M*, 292.0613).

(**7**; X = NO_2), m.p. 115.5—116.5 °C (lit.,[31] 118—119 °C); *m/z* 292 (M^+, 65%) and 155 (M^+ − NHAr, 100); δ($CDCl_3$) 8.15 (1 H, d, J_{PH} 5 Hz), 8.0—6.9 (9 H, m; includes δ 7.96, d, J_{HH} 9 Hz and δ 6.95, d, J_{HH} 9 Hz), and 3.85 (3 H, d, J_{PH} 11 Hz); δ_P(MeOH) 19.24 p.p.m.

(**6**; X = Cl), δ_P(MeOH) 18.93 p.p.m. and (**7**; X = Cl), δ_P(MeOH) 20.06 p.p.m. were prepared and characterised as part of an earlier investigation.[7]

The i.r. spectra (Nujol) of the compounds (**6**) and (**7**) all contained one or more peaks at 3 200—3 100 (NH) and at 1 225—1 200 cm^{-1} (P=O).

In g.l.c. the order of elution for the pairs of compounds was: X = MeO, (**7**) before (**6**) (3% OV 225); X = Me, (**7**) before (**6**) (3% OV 225); X = NO_2 (**6**) before (**7**) (1% OV 17); X = Cl, (**6**) before (**7**) (3% OV 17).

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