O-Sulphonyl-*N*-phosphoylhydroxylamines: Nucleophilic Attack at Nitrogen by Dimethyl Sulphide and Allyl Methyl Sulphide Leading to *N*-Phosphoyl Sulphilimines†

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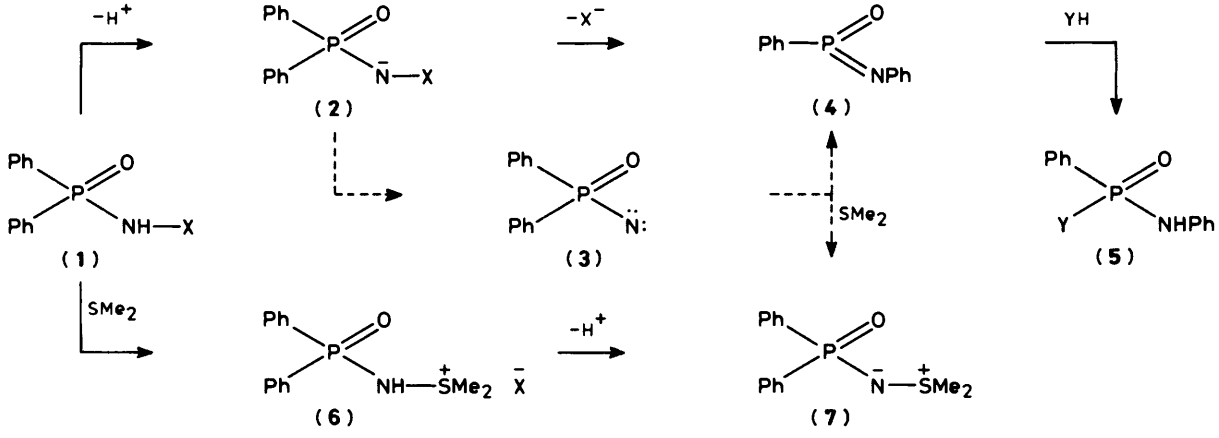
The *O*-sulphonyl-*N*-phosphoylhydroxylamines RR'P(O)NHX [R,R' = Ph or *p*-MeC_6H_4O; X = OMs or ONs] generally react with dimethyl sulphide and allyl methyl sulphide at room temperature in the absence of base. Nucleophilic attack at nitrogen, with displacement of the sulphonate anion, gives the protonated *N*-phosphoyl sulphilimine [*e.g.* (**6**)] which is converted into the free sulphilimine [*e.g.* (**7**)] on treatment with base. The allylic sulphilimines [*e.g.* (**9**)] are labile, undergoing [2,3]-sigmatropic rearrangement to *N*-phosphoyl-*N*-allylsulphenamides [*e.g.* (**10**)]. In the light of these results, the formation of some sulphilimine when the base-induced rearrangement of $Ph_2P(O)NHOMs$ is carried out in dimethyl sulphide need not be seen as evidence for a nitrene mechanism.

The *O*-sulphonyl-*N*-phosphinoylhydroxylamine (**1**; X = OMs) undergoes a Lossen-like rearrangement on treatment with base, to give, in high yield, products derived from the monomeric metaphosphonimidate (**4**) (Scheme), *e.g.* methyl phosphonamidate (**5**; Y = MeO) with sodium methoxide in methanol, and the phosphonic diamide (**5**; Y = Bu^{t}NH) with t-butylamine.[1] In principle, the metaphosphonimidate (**4**) could be formed from anion (**2**), the conjugate base of the substrate, either by concerted rearrangement or by way of the (singlet) nitrene intermediate (**3**). Dimethyl sulphide is known to be an efficient trap for several types of nitrene,[2,3] and recently it was used to trap phosphinoyl nitrenes generated photochemically from phosphinic azides.[4] The work now described had as its starting point an attempt to intercept a phosphinoyl nitrene during the base-induced rearrangement of (**1**; X = OMs).

as an authentic sample of the nitrene adduct, the sulphilimine (**7**).[4] The same minor product also accompanied the product of rearrangement (**5**; Y = MeO) when the methanesulphonate was treated with methanolic sodium methoxide in dimethyl sulphide; in this case it was isolated (preparative t.l.c.) and the sulphilimine structure (**7**) established beyond doubt. It is not unreasonable to infer that (**1**; X = OMs) reacts with base to give the nitrene (**3**) which then rearranges to the metaphosphonimidate (**4**); if the rearrangement is sufficiently rapid only a small part of the total nitrene will be trapped as the sulphilimine before it rearranges. We certainly do not discount this possibility, but we favour an alternative explanation for several reasons.

Firstly, whereas (**1**; X = OMs) is generally stable in solution in the absence of base, in dimethyl sulphide it was gradually



Scheme.

Results and Discussion

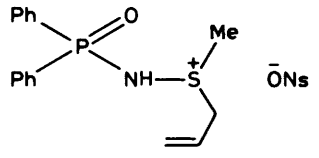
When the reaction of the methanesulphonate (**1**; X = OMs) with t-butylamine was carried out using dimethyl sulphide as the solvent, the phosphonic diamide (**5**; Y = Bu^{t}NH) was still the dominant product (90%). However, examination of the reaction mixture by t.l.c. and n.m.r. spectroscopy (^{31}P and ^1H) revealed a minor product (10%) having the same characteristics

converted into a salt-like compound the analysis for which was consistent with its formulation as the adduct (**6**; X = OMs); the latter was immediately converted into the sulphilimine (**7**) on treatment with base (aqueous NaOH or Bu^tNH_2) (Scheme). Thus it seems that dimethyl sulphide, acting as a nucleophile, can attack the substrate at nitrogen, displacing the methanesulphonate anion and forming the protonated sulphilimine. In the presence of base this nucleophilic attack may be competitive with the base-induced rearrangement, and lead to the sulphilimine without the intervention of a nitrene intermediate.

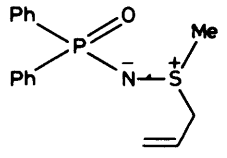
† Phosphoyl = phosphinoyl, phosphonoyl, or phosphoroyl. OMs = Methylsulphonyl. ONs = Nitrophenyl-*p*-sulphonyl.

Secondly, the nitrobenzenesulphonate (**1**; X = ONs), prepared from *N*-(diphenylphosphinoyl)hydroxylamine by brief treatment with *p*-nitrobenzenesulphonyl chloride in pyridine at 0 °C, behaved somewhat differently from the methanesulphonate. In particular, it reacted very quickly with t-butylamine in dimethyl sulphide to give exclusively the rearrangement product (**5**; Y = Bu^{t}NH) and none of the sulphilimine. If the reaction were proceeding *via* a nitrene intermediate, it is difficult to see how the nature of the leaving group could influence the extent to which dimethyl sulphide traps out the nitrene before it rearranges. For a non-nitrene mechanism, however, replacement of methanesulphonyl by the more electronegative nitrobenzenesulphonyl group could well assist the rearrangement more than the nucleophilic attack. While both reactions require the sulphonyl group to depart as the sulphonate anion, the rearrangement, but not the nucleophilic attack, also requires prior conversion of the substrate into its conjugate base (**2**); this conversion is likely to occur more readily for the nitrobenzenesulphonate than for the methanesulphonate.

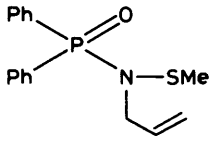
When dimethyl sulphide was replaced as the solvent by allyl methyl sulphide, the methanesulphonate (**1**; X = OMs) gave only the rearrangement product (**5**; Y = Bu^{t}NH) on treatment with t-butylamine. We attribute the absence of a sulphilimine (or related) product here to the reduced nucleophilicity of the sulphide—so that nucleophilic attack on the substrate can no longer compete effectively with the base-induced rearrangement—although it is true that this sulphide is also unlikely to be as efficient as dimethyl sulphide at intercepting any nitrene intermediate. With allyl methyl sulphide in the absence of base, the methanesulphonate (**1**; X = OMs) did not react at an appreciable rate at room temperature. The nitrobenzenesulphonate (**1**; X = ONs), on the other hand, was completely consumed within 3.6 h, to form a product (δ_P 29.4 p.p.m.) believed to be the sulphilimine salt (**8**) [low-field SMe signal (δ 3.29, s) in the ^{1}H n.m.r. spectrum]. Base converted this salt into a labile compound (δ_P 26.6 p.p.m.) which changed during 35 min



(**8**)



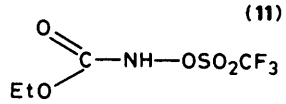
(**9**)



(**10**)

into a different, stable, compound (δ_P 35.5 p.p.m.). The stable product was isolated by chromatography and crystallisation and was found (M^+, 303; elemental analysis) to be isomeric with the sulphilimine (**9**). It appears to be the product (**10**) resulting from [2,3]-sigmatropic rearrangement of the sulphilimine, since one of the most prominent ions (50% relative abundance) in its mass spectrum corresponds to loss of thioformaldehyde ($M^+ - H_2CS$), and its ^{1}H n.m.r. spectrum shows the allylic protons to be coupled to phosphorus (δ_H 3.80, 2 H, dd, $J_{PH} \sim J_{HH}$ *ca.* 6 Hz), and the SMe group to be less deshielded (δ_H 2.14, 3 H, s), than would be expected in a sulphilimine. The pronounced tendency of allylic N-*sulphonyl* sulphilimines to undergo [2,3]-sigmatropic rearrangement is well documented in the literature.[3,5]

(**11**)



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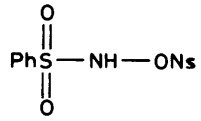
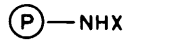


(**13**)

While the susceptibility of the sulphonates (**1**; X = OMs or ONs) to nucleophilic attack at nitrogen makes more difficult the task of establishing whether or not they rearrange *via* a nitrene, from a synthetic standpoint it could prove useful. Electrophilic aminating agents such as (**11**) have been used extensively to transfer the amino group (NH_2) to a wide range of nucleophiles.[6] Successful transfer of an alkoxycarbonyl- or sulphonylamino group is much less common, although it has been accomplished using compound (**12**)[7] or (**13**)[8] with dimethyl sulphide and other powerful nucleophiles such as triphenylphosphine.* Having found that the sulphonates (**1**; X = OMs or ONs) can transfer a phosphinoylamino group to a sulphide we therefore decided to examine some related compounds (**14a**, **b**; X = OMs, ONs) to see if phosphonoyl- and phosphorylamino groups can also be transferred.

With dimethyl sulphide the substrates (**14a**,**b**) gave initially the sulphilimine salts (**15a**,**b**) and then, on treatment with base, the free sulphilimines (**16a**,**b**). The products were formed in very high yield (^{31}P n.m.r. spectroscopy) but only the salt (**15a**; X = ONs) and the sulphilimine (**16a**) could be isolated as pure crystalline compounds, although the sulphilimine (**16b**) did form a crystalline derivative with picric acid. The ^{1}H n.m.r. spectra of the phosphonoyl compounds (**15a**) and (**16a**) displayed separate signals [$\Delta\delta$(CDCl$_3$) 0.11—0.15] for the two methyl groups attached to sulphur, presumably because non-planarity at sulphur combined with chirality at phosphorus makes them diastereotopic.



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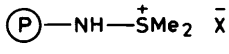

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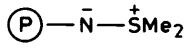
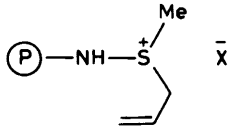
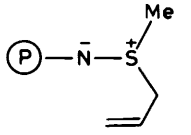


(**16**)



(**17**)



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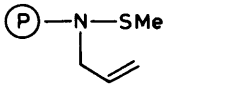
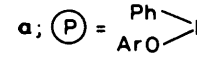
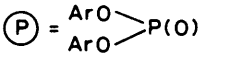


(**19**)

a; Ⓟ =  b; Ⓟ = 

(Ar = *p*-tolyl)

* The methanesulphonate (**1**; X = OMs) also reacts with triphenylphosphine to give the phosphinimine salt $Ph_2P(O)NH\overset{+}{P}Ph_3\bar{O}Ms$ [δ_P 22.2 and 17.1 p.p.m. (Found: C, 64.8; H, 5.2; N, 2.2. $C_{31}H_{29}NO_4P_2S$ requires C, 64.9; H, 5.1; N, 2.4%)] which with base is converted into the known free phosphinimine $Ph_2P(O)N{=}PPh_3$ (δ_P 14.3 and 13.5 p.p.m.).

The phosphonoyl and phosphoroyl nitrobenzenesulphonates (**14a,b**; X = ONs) reacted more rapidly with allyl methyl sulphide (1.75 h and 0.5 h respectively at room temperature) than did the phosphinoyl analogue (3.6 h), and even the methanesulphonates (**14a,b**; X = OMs) reacted quite readily (overnight). Apparently the susceptibility of the N atom to nucleophilic attack increases as the phosphorus substituent changes phosphinoyl ⟶ phosphonoyl ⟶ phosphoroyl, although to some extent the differing rates of reaction are probably due simply to differences in reactant solubility. The sulphilimine salts (**17a,b**) formed in these reactions, and the free sulphilimines (**18a,b**) obtained on treating them with base, were observed spectroscopically but with the exception of (**17a**; X = OMs) they were not isolated in a pure state. As with the phosphinoyl system, the sulphilimines rearranged to the *N*-allyl-*N*-thiomethyl amides (**19a,b**) which were purified by chromatography.

Experimental

Instrumentation was as previously described.[9] Unless otherwise indicated, ^{31}P N.m.r. chemical shifts are quoted (relative to 85% H_3PO_4) for solutions in CH_2Cl_2 or $CDCl_3$–CH_2Cl_2, i.r. frequencies for Nujol mulls, and t.l.c. data for separations on alumina. Reactions were carried out at room temperature (or as stated) with exclusion of moisture. Except for compound (**1**; X = ONs) the methods of preparation of the *N*-phosphoyl-*O*-sulphonylhydroxylamines have already been described.[1,10]

N-(*Diphenylphosphinoyl*)-O-(p-*nitrophenylsulphonyl*) *hydroxylamine* (**1**; X = ONs).—*N*-(Diphenylphosphinoyl)-hydroxylamine[1] (1.00 g, 4.3 mmol) was mixed thoroughly with pyridine (5 ml) at 0 °C and *p*-nitrobenzenesulphonyl chloride (1.46 g, 6.5 mmol) was added. The mixture was shaken at 0 °C for 10 min and was then quenched with iced water (50 ml). The crude product separated and was recrystallised from methanol to give the p-*nitrobenzenesulphonate* (**1**; X = ONs) (1.10 g, 61%), m.p. 142—143 °C (decomp.); $\nu_{max.}$ 3 060 (NH), 1 350 (NO_2), and 1 205 cm^{-1} (P=O); *m/z* 418 (M^+, 10%), 417 (15), 201 (55), 93 (45), and 92 (100); δ(CD_3SOCD_3) 10.90 (d, J_{PH} 6 Hz, NH), 8.4—8.0 (AA'BB' pattern centred at 8.22, $C_6H_4NO_2$), and 7.8—7.3 (Ph) (Found: C, 51.6, 51.4; H, 3.7, 3.6; N, 6.0, 7.55. $C_{18}H_{15}N_2O_6PS$ requires C, 51.7; H, 3.6; N, 6.7%. The reason for the inconsistent N analysis is unknown).

Reactions of N-*Phosphoyl*-O-*sulphonylhydroxylamines with Dimethyl Sulphide.*—(*a*) *With base present.* The sulphonate (**1**; X = OMs or ONs) was added with stirring to a large excess of dimethyl sulphide (50—100 mol equiv.) containing either t-butylamine (5 mol equiv.) or methanolic NaOMe (0.4M; 2 mol equiv.). Volatile material was removed under reduced pressure and the crude reaction product was analysed by n.m.r. spectroscopy (^1H and ^{31}P) and t.l.c. with the aid of authentic specimens of the rearrangement products (**5**; Y = Bu^{t}NH) and (**5**; Y = MeO)[1] and the sulphilimine (**7**).[4] A sample of the sulphilimine (**7**) was isolated by preparative t.l.c. (alumina; R_F *ca.* 0.2 using 6% MeOH in ether), and had i.r. and ^1H n.m.r. spectra identical with those of the authentic specimen.[4]

(*b*) *Without base present.* The appropriate sulphonate was stirred with a large excess of dimethyl sulphide until the solid had all dissolved and ^{31}P n.m.r. spectroscopy showed complete conversion into the sulphilimine salt. Excess of sulphide was evaporated under reduced pressure and the salt was crystallised if possible. The salt was then dissolved in CH_2Cl_2 and converted into the free sulphilimine by washing with water containing slightly more than the required amount of NaOH [also, in the case of (**6**; X = OMs), by adding t-butylamine]. The following compounds were obtained.

Salt (**6**; X = OMs), δ_P 29.4; m.p. 110—112 °C (from chloroform–ether); $\nu_{max.}$ 2 660 cm^{-1} (NH); δ($CDCl_3$) 8.0—7.2 (Ph), 7.13 (br, NH), 3.28 (s, SMe_2), and 2.43 (s, OMs) (Found: C, 48.4; H, 5.5; N, 3.65. $C_{15}H_{20}NO_4PS_2$ requires C, 48.2; H, 5.4; N, 3.75%). The recrystallised analytical sample showed no clear m.p.

Salt (**6**; X = ONs), δ_P 28.0 p.p.m.; m.p. 159—164 °C (solid not obtained crystalline); $\nu_{max.}$ 2 680 cm^{-1} (NH); δ($CDCl_3$–CD_3SOCD_3) 8.3—7.3 (ONs, Ph, and NH), and 3.20 (s, SMe_2).

Salt (**15a**; X = OMs), δ_P 17.7 p.p.m.; glassy solid; $\nu_{max.}$(CH_2Cl_2) *ca.* 2 560 br cm^{-1} (NH); δ($CDCl_3$) 8.1—7.3 (Ph and NH), 7.18 (MeC_6H_4O), 3.17 and 3.02 (both 3 H, s, SMe_2), 2.61 (s, OMs), and 2.28 (s, MeC_6H_4O).

Salt (**15a**; X = ONs), δ_P 17.1 p.p.m.; m.p. 112—115 °C (from dichloromethane–ether); $\nu_{max.}$ 2 720 cm^{-1} (NH); δ($CDCl_3$) 8.3—7.25 (ONs and Ph), 7.06 (s, MeC_6H_4O), 6.15 (br, NH + some H_2O), 3.19 and 3.08 (both 3 H, s, SMe_2), and 2.27 (s, MeC_6H_4O) (Found: C, 49.5; H, 4.5; N, 5.2. $C_{21}H_{23}N_2O_7PS_2$ requires C, 49.4; H, 4.5; N, 5.5%).

Salt (**15b**; X = OMs), δ_P −5.6 p.p.m.; not obtained crystalline; $\nu_{max.}$ 2 630 cm^{-1} (NH); δ($CDCl_3$) 7.66 (br, NH), 7.12 (8 H, s, MeC_6H_4O), 3.02 (s, SMe_2), 2.72 (s, OMs), and 2.29 (6 H, s, MeC_6H_4O).

Salt (**15b**; X = ONs), δ_P −5.9 p.p.m.; not obtained crystalline; δ($CDCl_3$) 8.3—7.8 (NH and ONs, AA'BB' pattern centred at 8.02), 7.06 (8 H, s, MeC_6H_4O), 3.01(s, SMe_2), and 2.27 (6 H, s, MeC_6H_4O).

Sulphilimine (**7**), δ_P 26.4; spectra as for the authentic specimen.[4]

Sulphilimine (**16a**), δ_P 24.4 p.p.m.; m.p. 79—81 °C [crystallised slowly from chloroform–ether (1 : 10) at −20 °C]; *m/z* 307 (M^+, 12%), 200 [(M^+ − OC_6H_4Me), 100], and 167 (60); δ($CDCl_3$) 7.95—7.2 (Ph), 6.98 (s, MeC_6H_4O), 2.60 and 2.48 (both 3 H, s, SMe_2), and 2.22 (s, MeC_6H_4O) (Found: C, 58.8; H, 6.0; N, 4.4. $C_{15}H_{18}NO_2PS$ requires C, 58.6; H, 5.9; N, 4.6%).

Sulphilimine (**16b**), δ_P 4.6 p.p.m.; oil; *m/z* 337 (M^+, 12%), 230 [(M^+ − OC_6H_4Me), 70], and 167 (100); δ($CDCl_3$) 7.06 (8 H, MeC_6H_4O), 2.48 (s, SMe_2), and 2.27 (6 H, s, MeC_6H_4O). The derivative with picric acid had m.p. 98—100 °C (from chloroform–ether); $\nu_{max.}$ 2 630 cm^{-1} (NH); δ($CDCl_3$) 8.92 (2 H, s, picrate), 7.63 (s, NH + some H_2O), 7.05 (8 H, s, MeC_6H_4O), 2.72 (s, SMe_2). and 2.28 (6 H, s, MeC_6H_4O) (Found: C, 46.6; H, 4.15; N, 9.6. $C_{22}H_{23}N_4O_{10}PS$ requires C, 46.6; H, 4.1; N, 9.9%).

Reactions of N-*Phosphoyl*-O-*sulphonylhydroxylamines with Allyl Methyl Sulphide.*—(*a*) *With base present.* The sulphonate (**1**; X = OMs) was added to an excess of an equimolar mixture of allyl methyl sulphide and t-butylamine. Analysis of the reaction mixture by ^{31}P n.m.r. spectroscopy after 1 h showed only one product (δ_P 10.5), and the phosphonic diamide (**5**; Y = Bu^{t}NH) was isolated by crystallisation, m.p. 176—177 °C (lit.,[1] 176—178 °C), spectra as for the authentic sample.[1]

(*b*) *Without base present.* The sulphonates were stirred with an excess of allyl methyl sulphide (diluted with an equal volume of CH_2Cl_2 in the case of the nitrobenzenesulphonates to increase their solubility) until reaction was complete (^{31}P n.m.r. spectroscopy), except that compound (**1**; X = OMs) did not react and was recovered unchanged after 2 days. Evaporation of volatile material under reduced pressure usually left the sulphilimine salts as foams which could not be purified but which gave reasonable ^1H n.m.r. spectra (notably relatively low-field singlets, in the range δ 3.29—2.93, for the SMe groups). Exceptionally, the *salt* (**17a**; X = OMs) was obtained as a crystalline solid, δ_P 17.9 and 17.3 p.p.m. (mixture of diastereoisomers), m.p. 101—103 °C (from CH_2Cl_2–ether); $\nu_{max.}$ 2 630 cm^{-1} (NH); δ($CDCl_3$) 8.65 (br s, NH), 8.1—7.3 (Ph), 7.15 (MeC_6H_4O), 5.7—5.2 ($CH{=}CH_2$), 4.6—4.0 (allylic CH_2), 3.09 and 2.94 (total 3 H; 2 × s of similar intensity; SMe groups in

diastereoisomers), 2.66 (3 H, s, OMs), and 2.27 (3 H, s, MeC_6H_4O) (Found: C, 49.9; H, 5.7; N, 3.1. $C_{18}H_{24}NO_5PS_2$ requires C, 50.3; H, 5.6; N, 3.3%). The salts were dissolved in dichloromethane and were washed with water containing slightly more than the required amount of NaOH to give the free sulphilimines. These rearranged at room temperature and were not isolated, although for compound (**18b**) the rearrangement was comparatively slow and addition of picric acid gave the crystalline *sulphilimine picrate*; m.p. 79.5—81.5 °C (from tetrachloromethane); δ($CDCl_3$) 8.98 (2 H, s, picrate), 7.92 (br, NH + some H_2O), 7.08 (8 H, s, MeC_6H_4O), 5.9—5.25 (3 H, m, $CH{=}CH_2$), 3.73 (2 H, d, J_{HH} 6 Hz, allylic CH_2), 2.64 (3 H, s, SMe), and 2.28 (6 H, s, MeC_6H_4O) (Found: C, 48.2; H, 4.3; N, 9.2. $C_{24}H_{25}N_4O_{10}PS$ requires C, 48.65; H, 4.25; N, 9.5%).

The rearrangement products were isolated by flash chromatography (silica) and characterised as shown below.

N-*Allyl*-N-(*thiomethyl*)*diphenylphosphinic amide* (**10**), δ_P 35.5 p.p.m.; m.p. 70—72 °C [from light petroleum (b.p. 60—80 °C)]; *m/z* 303 (M^+, 20%), 257 [($M^+ - H_2CS$), 50], 202 (70), and 201 (100); δ($CDCl_3$) 7.9—7.3 (Ph), 5.90 (1 H, ddt, J_{HH} 9, 17, and 6 Hz, CH=), 5.18 (1 H, d, J_{HH} 17 Hz), and 5.15 (1 H, d, J_{HH} 9 Hz) ($=CH_2$), 3.80 (2 H, dd, $J_{PH} \sim J_{HH}$ *ca.* 6 Hz, allylic CH_2), and 2.14 (s, SMe) (Found: C, 63.7; H, 6.05; N, 4.6. $C_{16}H_{18}NOPS$ requires C, 63.35; H, 6.0; N, 4.6%).

N-*Allyl*-N-(*thiomethyl*)*phenyl*(p-*methylphenoxy*)*phosphinic amide* (**19a**), δ_P 21.2; an oil that decomposed on attempted purification; *m/z* 333 (M^+, 90%), 287 [($M^+ - H_2CS$), 50], 231 (55), 146 (55), and 91 (100); δ($CDCl_3$) 8.1—7.35 (Ph), 7.10 (MeC_6H_4O), 5.69 (1 H, ddt, J_{HH} 10, 17, and 6 Hz, CH=), 5.13 (1 H, d, J_{HH} 17 Hz), 5.08 (1 H, d, J_{HH} 10 Hz) ($=CH_2$), 3.95 (2 H, dd, J_{PH} 8, J_{HH} 6 Hz, allylic CH_2), 2.28 (s, MeC_6H_4O), and 1.96 (s, SMe) (Found: M^+, 333.0952. $C_{17}H_{20}NO_2PS$ requires *M*, 333.0952).

N-*Allyl*-N-(*thiomethyl*)-*bis*(p-*methylphenoxy*)*phosphinic amide* (**19b**), δ_P 0.6 p.p.m.; an oil that decomposed on attempted distillation; *m/z* 363 (M^+, 100%) and 317 [($M^+ - H_2CS$), 45]; δ($CDCl_3$) 7.08 (8 H, s, MeC_6H_4O), 5.72 (1 H, ddt, J_{HH} 17, 10, and 6 Hz, CH=), 5.16 (1 H, d, J_{HH} 17 Hz) and 5.11 (1 H, d, J_{HH} 10 Hz) ($=CH_2$), 3.94 (2 H, dd, J_{PH} 9, J_{HH} 6 Hz, allylic CH_2), 2.37 (3 H, s, SMe), and 2.27 (6 H, s, MeC_6H_4O) (Found: M^+ 363.1060. $C_{18}H_{22}NO_3PS$ requires *M*, 363.1058).

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