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DIARYLPHOSPHINIC AZIDES

PHOTOCHEMICAL REACTIONS INCLUDING REARRANGEMENT IN METHANOL

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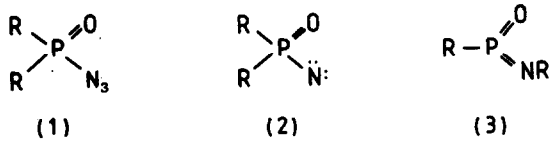
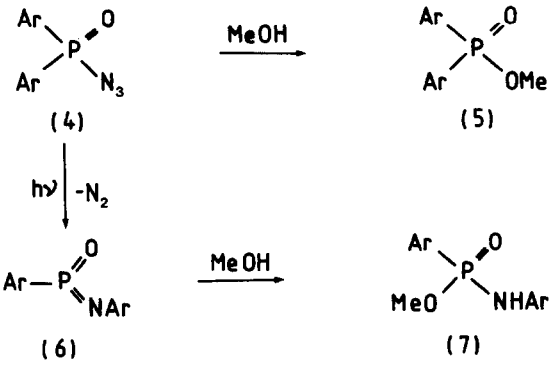
Abstract—On photolysis in methanol the diarylphosphinic azides $Ar_2P(O)N_3$ (Ar = phenyl, *p*-tolyl, *p*-anisyl, *p*-chlorophenyl) rearrange with loss of nitrogen to form (monomeric) metaphosphonimidates which are trapped by the solvent to give methyl NP-diarylphosphonamidates (7) (41–53%). Diarylphosphinic amides (18–42%) are also usually formed, presumably from (triplet) nitrenes. The limited evidence available suggests that the rearrangements take place directly from the photo-excited azides rather than via (singlet) nitrene intermediates. One of the products of rearrangement, methyl NP-di(*p*-chlorophenyl)phosphonamidate, suffers extensive photochemical dechlorination giving methyl N-phenyl-P-*p*-chlorophenylphosphonamidate.

Dialkylphosphinic azides (1) decompose with loss of nitrogen when photolysed in protic solvents.[1] Some product formally derived from the dialkylphosphinyl nitrene (2) may be obtained but the major reaction pathway is usually the migration of an alkyl group from P to N and reaction of the resulting monomeric metaphosphonimidate (3) with solvent.[1] It has not been established whether the metaphosphonimidate is formed via a nitrene or directly from the azide with simultaneous rearrangement and expulsion of nitrogen. The present work was undertaken to see whether diarylphosphinic azides behave similarly on photolysis, and in particular to investigate the parts played by nitrenes and metaphosphonimidates.



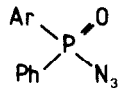
(1) (2) (3)



Scheme 1.

RESULTS AND DISCUSSION

The diarylphosphinic azides[2] (4, Ar = phenyl, *p*-tolyl, *p*-anisyl, or *p*-chlorophenyl) were prepared from the appropriate phosphinic chlorides and sodium azide in acetonitrile at room temperature. They were irradiated (medium pressure mercury lamp; quartz vessel) in methanol at 7–10° until evolution of nitrogen ceased, and the products were isolated by chromatography. In each case solvolysis of the azide competed with nitrogen-eliminating decomposition causing the methyl phosphinate (5) to be formed in a yield ranging from 3.5% (Ar = *p*-anisyl) to 33% (Ar = *p*-tolyl or *p*-chlorophenyl). Control dark reactions showed that much of the observed solvolysis could result from azide in the ground state, although some contribution from photo-excited azide can not be excluded. The major product, isolated in 41–53% yield, was always the methyl NP-diarylphosphonamidate (7) formed by migration of an aryl group to N (as in the Curtius rearrangement of an acyl azide[3]) and trapping of the resulting metaphosphonimidate (6) by the methanol solvent. In the case of the azide (4, Ar = *p*-chlorophenyl) the isolated methyl phosphonamidate was an unequal mixture of two compounds (glc). An authentic sample of the expected product (7, Ar = *p*-chlorophenyl) was prepared from *p*-chlorophenylphosphonic dichloride, by sequential reaction with methanol and *p*-chloroaniline, and was found (glc) to correspond to the minor component of the mixture. The mass spectrum of the photolysis product, together with the results of elemental analysis, suggested that the major component lacked one Cl atom. If dechlorination occurred before normal azide decomposition the resulting unsymmetrical azide (8) could rearrange with migration of either phenyl or *p*-chlorophenyl to N. However, the mass spectrum of the product contained abundant ions of *m/e* 189 and 191 $[ClC_6H_4\overset{+}{P}(O)OMe]$ but not 155 $[\overset{+}{P}(O)OMe]$, pointing to the presence of 9 but not 10. Moreover, degradation of the product with methanolic HCl gave dimethyl *p*-chlorophenylphosphonate but not dimethyl phenylphosphonate, although aniline and *p*-chloroaniline were both formed. Finally an authentic sample of 9 was prepared and shown (glc, NMR) to correspond to the major component in the photolysis product. Thus it seems likely that dechlorination occurred only after rearrangement had transferred the *p*-chlorophenyl group from P to N.



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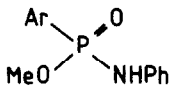

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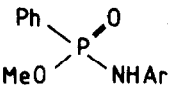


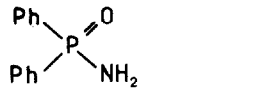
(10)

(Ar = p- Chlorophenyl)

Photochemical dehalogenation of aryl halides is not uncommon[4] but it does not seem to have been observed before in phosphorus chemistry. We therefore looked briefly at the model compounds **12** (X = Ph or MeO) to confirm the ready loss of Cl from *p*-chloroanilides of P(V) acids. Irradiation of the *p*-chloroanilide **12** (X = Ph) in methanol for 5 hr, under conditions similar to those used for the azide photolysis, gave the anilide **13** (X = Ph). After 3 hr, the time employed for the azide photolysis, dechlorination was about 80% complete. An unexpected minor product (*ca* 10%), the dimethyl phosphonate **11** (X = Ph), was detected by glc. Since the appearance of this product was directly related to the disappearance of starting material, it seems that it was formed from the *p*-chloroanilide but not from the anilide. A separate experiment confirmed the relative photostability of the anilide **13** (X = Ph). The second model compound **12** (X = MeO) lost Cl even more quickly, and had been completely converted into the anilide **13** (X = MeO) after 1.3 hr. In this case **11** (X = MeO) was not detected.

When our work was practically complete, a preliminary account of some interesting photochemical reactions of diphenylphosphinic azide appeared from Majoral *et al.*[5] They have trapped the monomeric metaphosphonimidate **6** (Ar = Ph) with various reagents, including methanol, but they do not indicate the yields of adducts nor whether any unrearranged products were obtained. Two such products were found in our photolysis of diphenylphosphinic azide in methanol, namely the amide **14** (18%) and the N-methoxyamide **15** (2.5%). These are formally derived from the triplet and singlet nitrenes respectively, by H- abstraction and insertion. The azides **4** (Ar = *p*-tolyl or *p*-anisyl) gave substantially more of the corresponding amides (26 and 42% respectively), but in the case of **4** (Ar = *p*-chlorophenyl) we found no evidence of amide, even though an authentic sample was available. This surprising result may be connected with the fate of the rearrangement product **7** (Ar = *p*-chlorophenyl), since dechlorination generates HCl. Phosphinic amides are notably susceptible to hydrolysis under very mild acid conditions,[6,7] and any di(*p*-chlorophenyl)phosphinic amide formed in the azide photolysis would be likely to suffer acid-catalysed methanolysis. Certainly the high yield of methyl di(*p*-chlorophenyl)phosphinate can accommodate this explanation.

A question of particular concern is whether metaphosphonimidates (**6**) are formed by rearrangement of phosphinyl nitrenes, presumably in their singlet states, or directly from phosphinic azides. Dimethyl sulphoxide (DMSO) is known to be effective as a trap for sulphonyl nitrenes,[8] and Kameyama *et al.*[9] have reported that the ammonium ylid **16** on photolysis (or thermolysis) in DMSO gives the sulphoximine **17** (29%) and diphenylphosphinic amide **14** (51%). These products are formally derived from singlet and triplet diphenylphosphinyl nitrene respectively. Having confirmed this result, we photolysed diphenylphosphinic azide in DMSO. The sulphoxime **17** and diphenylphosphinic amide were obtained, but only in very low yield (2.8 and 4.7% respectively), with diphenylphosphinic acid (82%) as the dominant product. This acid could in principle be formed simply by hydrolysis of the azide, but as rigorous precautions were taken to exclude moisture an alternative explanation seems necessary. Many reactions are known in which DMSO acts as a nucleophile, ultimately transferring its O atom to an electrophilic centre,[10] and something similar is probably happening here.† Whatever the precise details, DMSO is obviously not helpful in determining whether or not a nitrene trap suppresses the formation of metaphosphonimidate.



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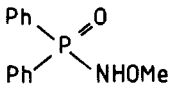

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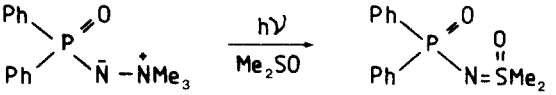
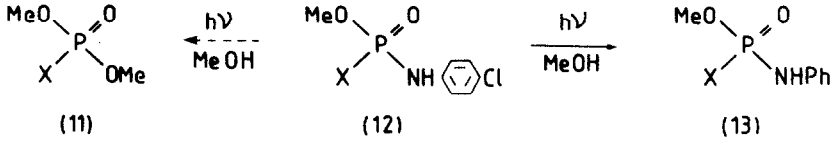


(16) (17)

An alternative approach would involve generating



(11) (12) (13)

Scheme 2.

†If water were responsible for the $Ph_2P(O)OH$, then the presence of methanol should lead instead to $Ph_2P(O)OMe$. In fact we found that photolysis of the azide in DMSO containing MeOH (*ca.* 0.6%) still gave $Ph_2P(O)OH$ and no $Ph_2P(O)OMe$. [$PhP(O)(OH)_2$ was an unexpected product in this case]. It may be signficant that other workers obtained $Ph_2P(O)OH$ (98%) from the thermolysis of diphenylphosphinic azide in DMSO (F. Weissbach and W. Jugelt, *J. prakt. Chem.* **317**, 394 (1975)).

phosphinyl nitrenes from different precursors and seeing if they form the same rearrangement products as are obtained from phosphinic azides. To date, only one non-azide source of phosphinyl nitrenes is known, namely the ammonium yield **16**. We therefore photolysed **16** in methanol. Diphenylphosphinic amide was the only substantial product detected, methyl NP-diphenylphosphonamidate **7** (Ar = Ph) was definitely absent (< 1%), and the ^{1}H NMR spectrum of the crude product showed no significant N-Ph resonance. If the ylid **16** does indeed form (singlet) diphenylphosphinyl nitrene, and that nitrene is not different from the one formed by diphenylphosphinic azide, then one is forced to conclude that the metaphosphonimidate is formed directly from the photo-excited azide by concerted loss of nitrogen and rearrangement.

EXPERIMENTAL

Instrumentation was as previously described.[11] Small scale distillations were carried out with a Kugelrohr apparatus and the stated b.p.s are oven temps. Chromatography employed neutral alumina. Glc analyses were performed on a Pye 104 flame-ionisation chromatograph 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'. MeOH was purified by distillation from its Mg salt, and dimethyl sulphoxide by drying over calcium hydride and distilling under reduced pressure. Petroleum refers to the fraction b.p. 60–80°.

Diarylphosphinic acids. Diphenyl, di-*p*-tolyl, and di-*p*-anisylphosphinic acids were prepared by methods similar to those previously described.[11,12] For di(*p*-chlorophenyl)phosphinic acid, diethyl phosphite was treated with *p*-chlorophenylmagnesium bromide (general method of Kosolapoff and Struck[13]) to give di(*p*-chlorophenyl)phosphine oxide (92%) which was partially purified by crystallisation from toluene, m.p. 122–125° (lit.,[14] 131–133°), ν_{max} (Nujol) 2360 (PH), 1195 and 1185 cm^{-1} (P=O), δ(CDCl$_3$) 8.0–7.3 (8H, m) and 7.92 (1H, d, J_{PH} 475 Hz) and then oxidized as follows (rather than with bromine[13]). The phosphine oxide (11.6 g, 0.043 mol) in CH_2Cl_2 (30 ml) was stirred with 30% H_2O_2 soln (25 ml) for 24 hr. The aqueous layer was make alkaline by addition of 2M NaOH, separated, and acidified to give a ppt of di(*p*-chlorophenyl)phosphinic acid (7.6 g, 0.027 mol, 64%), m.p. 134–137° (lit.,[15,16] 133–135 or 145–146°), ν_{max} (Nujol) 2650 br, 2150 br and 1680 (OH), and 1180 cm^{-1} (P=O), δ(CDCl$_3$) 11.8 br (1H, s) and 8.0–7.2 (8H, m).

Diarylphosphinic chlorides. The appropriate phosphinic acid was treated with an excess of gently refluxing $SOCl_2$ (no additional solvent) for 2 hr. Volatile material was removed under reduced pressure and the residue was distilled in a Kugelrohr apparatus. The following were prepared: Diphenylphosphinic chloride, b.p. 187–191° (oven temp) at 0.25 mmHg (lit,[17] 135–140° at 0.01 mmHg), di-*p*-tolylphosphinic chloride, b.p. 179–182° (oven temp) at 0.2 mmHg (lit,[2] 164–167° at 0.05 mmHg), di-*p*-anisylphosphinic chloride, b.p. 206° (oven temp) at 0.3 mmHg (lit,[18] 216° at 0.05 mmHg), and di(*p*-chlorophenyl)phosphinic chloride, b.p. 175–178° (oven temp) at 0.3 mmHg (lit,[2] 183–187° at 0.2 mmHg), solidified when cold.

Diarylphosphinic azides. The appropriate phosphinic chloride (8 mmol) and sodium azide (12 mmol) were stirred in dry acetonitrile (10 ml) at room temp for *ca* 16 hr. Insoluble matter was removed and the filtrate was concentrated under reduced pressure and then distilled in a Kugelrohr apparatus. This afforded diphenylphosphinic azide (90%), b.p. 160–163° (oven temp) at 0.05 mmHg (lit,[2] 137–140° at 0.05 mmHg), di-*p*-tolylphosphinic azide (54%), b.p. 137–143° (oven temp) at 10^{-4} mmHg (lit,[2] 190–195° at 0.5 mmHg), *di-p-anisylphosphinic azide* (48%), b.p. 130–136° (oven temp) at 0.007 mmHg (slight decomposition occured during distillation and no attempt was made to obtain elemental analysis), δ(CDCl$_3$) 7.85 (4H, dd, J_{PH} 12, J_{HH} 8 Hz), 7.08 (4H, dd, J_{PH} 4, J_{HH} 8 Hz), and 3.87 (6H, s), δ_p (CH_2Cl_2) 30.5, and di(*p*-chlorophenyl)phosphinic azide (70%), b.p. 167–172° (oven temp) at 0.05 mmHg (lit,[2] 160–165° at 0.005 mmHg). The azides all gave intense absorptions at *ca* 2150 (N_3) and 1270–1230 cm^{-1} (2 peaks, P=O).

Trimethylammonium-N-diphenylphosphinylimine. This compound was prepared by essentially the method of Kameyama *et al.*[9] 1,1-Dimethyl-2-diphenylphosphinylhydrazine (53%; 2 hr reaction time) had m.p. 167–169° (lit,[9,19] 178.2–178.5 or 167–168°), δ(CDCl$_3$) at 8.25–7.3 (10H, m), 3.75 br (1H), and 2.63 (6H, s) after drying under vacuum and crystallising from toluene. It was heated gently under reflux with MeI (2 equiv) in a small volume of EtOH for ≥ 4 hr, when the NMR spectrum [δ(CDCl$_3$) 8.25–7.35 (10H, m) and 3.85 (9H, s)] showed complete conversion of the starting material to 1,1,1-trimethyl-2-diphenylphosphinylhydrazinium iodide. This salt was not purified but was treated directly with 10% NaOHaq. The product was extracted into $CHCl_3$ and crystallised from toluene to give trimethylammonium-N-dimethylphosphinylimine (78%), m.p. 172–174° (lit,[9] 178.3–178.5°), δ(CDCl$_3$) 8.2–7.2 (10H, m) and 3.38 (9H, s), δ_p (CDCl$_3$) 19.8.

p-Chlorophenylphosphonic dichloride

(a) Following the procedure of Gefter,[20] chlorobenzene was heated with PCl_3 and $AlCl_3$ to give chlorophenylphosphonous dichloride (65%), b.p. 66–80° at 0.1 mmHg (lit,[20] 90–92° at 1-2 mmHg); the IR spectrum contained a strong absorption at 815 (*p*-$ClC_6H_4PCl_2$) but only very weak absorptions at 1430 and 1035 (*o*-isomer) and 780 cm^{-1} (*m*-isomer).[20,21]

(b) Chlorophenylphosphonous dichloride was hydrolysed (H_2O–EtOH–HCl)[21] and the product crystallised from water to give isomerically-pure *p*-chlorophenylphosphonous acid (56%), m.p. 130–132.5° (lit,[21] 131–132°), ν_{max} (Nujol) 2600, 2100 and 1650 (all broad, OH) and 2420 cm^{-1} (PH).

(c) The phosphonous acid was treated with PCl_3 as in the published procedure[21] to give isomerically-pure (IR) *p*-chlorophenylphosphonous dichloride (10 g, 27%) which was dissolved in CCl_4 (8 ml) and stirred at −10° while sulphuryl chloride (6 g) was added dropwise. After 3 hr at room temp, volatile matter was removed under reduced pressure and the residue distilled to give *p*-chlorophenylphosphonic dichloride (10.0 g, 93%), b.p. 90–100° at 0.3 mmHg (lit,[22] 152° at 15 mm), ν_{max} (film) 1275 and 1260 cm^{-1} (P=O).

Preparation of authentic samples used in analysis of the products of photochemical reactions

Methyl N-aryl-P-arylphosphonamidates. These were prepared by methods based on that of Hershman and Audrieth[23] for methyl NP-diphenylphosphonamidate. Typically, a mixture of MeOH (0.14 g, 4.4 mmol) and Et_3N (0.44 g, 4.4 mmol) in ether was added slowly with stirring to *p*-chlorophenylphosphonic dichloride (1.0 g, 4.3 mmol) in ether. After a further 1 hr the mixture was filtered and *p*-chloroaniline (1.11 g, 8.7 mmol) in ether was added slowly to the filtrate. The soln was boiled under reflux for 2 hr, filtered, and concentrated. The residue dissolved in CH_2Cl_2 was washed with very dilute HCl, dried ($MgSO_4$), and chromatographed on alumina (eluent ether containing 1–2.5% MeOH) to give *methyl* NP-*di*(p-*chlorophenyl*)*phosphonamidate* (1.07 g, 3.4 mmol, 79%), *m/e* 315, 317 and 319 (M^+, 100), 189 and 191 (M^+–ClC_6H_4NH, 70%), and 111 and 113 ($ClC_6H_4^+$, 35%), ν_{max} (film) 3160 (NH), 1210 (P=O), and 1030 cm^{-1} (POMe), δ(CCl_4) 8.58 br (1H, d, J_{PH} 4 Hz), 7.74 (2H, dd, J_{PH} 13, J_{HH} 8 Hz), 7.34 (2H, dd, J_{PH} 4, J_{PH} 8 Hz), 6.94 (4H, AA'BB' pattern), and 3.83 (3H, d, J_{PH} 12 Hz). This material was obtained as a very viscous liquid and resisted all attempts at crystallisation. It distilled, b.p. 170° (oven temp) at 0.07 mmHg, with slight decomposition and could not be obtained in a state appropriate for elemental analysis.

Methyl N-phenyl-P-p-chlorophenylphosphonamidate, m/e 281 and 283 (M^+, 100), 189 and 191 (M^+–PhNH, 45), and 111 and 113 ($ClC_6H_4^+$, 30%), ν_{max} (film) 3160 (NH), 1220 (P=O), and 1035 cm^{-1} (POMe), δ (CCl_4) 8.57 br (1H, d, J_{PH} 5 Hz), 7.76 (2H, dd, J_{PH} 13, J_{HH} 8 Hz), 7.26 (2H, dd, J_{PH} 4, J_{HH} 8 Hz), 7.15–6.8 (5H, m, dominated by peak at 6.97, NPh), and 3.85 (3H, d, J_{PH} 12 Hz) was prepared as above but with aniline in place of *p*-chloroaniline and without heating. It was also an

extremely viscous liquid that could not be crystallised. It distilled at 184–186° (oven temp) at 0.1 mmHg (Found: C, 54.8; H, 4.75; N, 4.7. $C_{13}H_{13}ClNO_2P$ requires: C, 55.4; H, 4.65; N, 5.0; $C_{13}H_{13}ClNO_2P.0{\cdot}2H_2O$ requires: C, 54.8; H, 4.7; N, 4.9%).

Methyl N-*p*-chlorophenyl-P-phenylphosphonamidate, *m/e* 281 and 283 (M^+, 100), 155 ($M^+ - ClC_6H_4NH$, 70), and 77 ($C_6H_5^+$, 65%), ν_{max} (Nujol) 3110 (NH) and 1210 cm^{-1} (P=O), $\delta(CDCl_3)$ 8.0–7.2 (6H, m, Ph and NH), 6.90 (4H, AA'BB' pattern, NC_6H_4Cl), and 3.80 (3H, d, J_{PH} 12 Hz) was similarly prepared using phenylphosphonic dichloride and *p*-chloroaniline with pyridine in place of Et_3N. It crystallised from ether (with difficulty) and had m.p. 124–5° (lit,[24] 130–131°); the m.p. was not changed by repeated crystallisation.

Dimethyl N-p-*chlorophenylphosphoramidate.* A mixture of *p*-chloroaniline hydrochloride (8.22 g, 50 mmol) and $POCl_3$ (30 ml) was boiled gently under reflux for 3 hr. On cooling a crystalline mass formed which was washed with petroleum and recrystallised from a small volume of benzene to give N-*p*-chlorophenylphosphoramidic dichloride (6.23 g, 27 mmol, 54%), m.p. 104–106° (lit,[25] 107°). A portion of this product (5.00 g, 23 mmol) dissolved in ether was added dropwise with stirring to 1.5M MeONa soln (31 ml). After a further 1 hr at room temp standard work-up and crystallisation from toluene afforded dimethyl N-*p*-chlorophenylphosphoramidate (2.87 g, 13 mmol, 57%), m.p. 95–96° (lit,[26] 97.5°), ν_{max} (Nujol) 3130 (NH) and 1225 cm^{-1} (P=O), $\delta(CDCl_3)$ 7.47 br (1H, d, J_{PH} 10 Hz), 7.02 (4H, AA'BB' pattern), and 3.73 (6H, d, J_{PH} 12 Hz).

Dimethyl N-*phenylphosphoramidate.* Dimethyl phosphorochloridate,[27] b.p. 74–76° at 12 mmHg (lit,[27] 80° at 18 mm), $\delta(CCl_4)$ 3.82 (d, J_{PH} 13 Hz) was treated with aniline (1 equiv) and Et_3N (1 equiv) in refluxing benzene for 3 hr. Standard work-up and repeated crystallisation from ether–petroleum (1:1) gave dimethyl N-phenylphosphoramidate (28%), m.p. 85–86° (lit,[28] 88°), ν_{max} (Nujol) 3160 (NH) and 1225 cm^{-1} (P=O), $\delta(CDCl_3)$ 7.4–6.9 (5H, m), 6.75 br (1H, d, J_{PH} 9 Hz), and 3.57 (6H, d, J_{PH} 11 Hz).

Methyl diarylphosphinates. In general these were prepared by adding an excess of diazomethane in ether to a stirred suspension of the phosphinic acid in ether at 0°. Distillation (Kugelrohr) gave *methyl di-p-tolylphosphinate*, b.p. 174° (oven temp) at 0.5 mmHg, m.p. 68–69°, *m/e* 260 (M^+, 60%) and 259 (100%), δ ($CDCl_3$) 7.57 (4H, dd, J_{PH} 12, J_{HH} 8 Hz), 7.05 (4H, dd, J_{PH} 3, J_{HH} 8 Hz), 3.62 (3H, d, J_{PH} 10 Hz), and 2.25 (6H, s) (Found: C, 69.5; H, 6.55. $C_{15}H_{17}O_2P$ requires: C, 69.2; H, 6.6%). *Methyl di-p-anisylphosphinate*, b.p. 192° (oven temp) at 0.15 mmHg, m.p. 106.5–108°, *m/e* 292 (M^+, 100%) and 291 (65%), $\delta(CDCl_3)$ 7.80 (4H, dd, J_{PH} 12, J_{HH} 8 Hz), 7.00 (4H, dd, J_{PH} 3, J_{HH} 8 Hz), 3.87 (6H, s), and 3.76 (3H, d, $J_{PH} \sim 10$ Hz) (Found: C, 61.6; H, 5.7 $C_{15}H_{17}O_4P$ requires: C, 61.6; H, 5.85%); and methyl di(*p*-chlorophenyl)phosphinate, b.p. 152–158° (oven temp) at 0.15 mmHg, m.p. 92.5–93.5° (lit,[29] 87.5–88.5°), *m/e* 300, 302 and 304 (M^+, 80%), 299, 301 and 303 ($M^+ - 1$, 100%), $\delta(CCl_4)$ 8.1–7.4 (8H, m) and 3.73 (3H, d, J_{PH} 11 Hz) (Found: C, 51.7; H, 3.6. Calc. for $C_{13}H_{11}Cl_2O_2P$: C, 51.85; H, 3.7%).

Methyl diphenylphosphinate, b.p. 165–169° (oven temp) at 0.8 mmHg (lit,[30] 139–140° at 0.34 mmHg), m.p. 55–57°, $\delta(CCl_4)$ 7.8–7.2 (10H, m) and 3.63 (3H, d, J_{PH} 11 Hz), was prepared from diphenylphosphinic chloride with MeOH and Et_3N.

The IR spectra of all the alkyl phosphinates (in Nujol) contained peaks at *ca* 1230 (P=O) and 1040 cm^{-1} (POMe).

Diarylphosphinic amides. Diphenyl and di-*p*-tolylphosphinic amides were available from previous work.[12] The following were similarly prepared from the appropriate diarylphosphinic chloride and ammonia: *Di-p-anisylphosphinic amide*, m.p. 138–139° (from toluene), ν_{max} (Nujol) 3400–3000 (NH) and 1170 cm^{-1} (P=O), $\delta(CDCl_3)$ 7.92 (4H, dd, J_{PH} 12, J_{HH} 8 Hz), 6.98 (4H, dd, J_{PH} 3, J_{HH} 8 Hz), 3.88 (6H, s), and 3.15 br (2H, s) (Found: C, 60.7; H, 5.8; N, 5.0. $C_{14}H_{16}NO_3P$ requires: C, 60.6; H, 5.8; N, 5.05%), and *di(p-chlorophenyl)phosphinic amide*, m.p. 169–171.5° (from toluene), *m/e* 285, 287 and 289 (M^+, 75%), 284, 286 and 288 ($M^+ - 1$, 100%), ν_{max} (Nujol) 3320, 3230, 3110 (NH) and 1165 cm^{-1} (P=O), $\delta(CDCl_3)$ 7.85 (4H, dd, J_{PH} 12, J_{HH} 8 Hz), 7.42 (4H, dd, J_{PH} 3, J_{HH} 8 Hz), and 3.90 br (2H, s) (Found: C, 50.2; H, 3.6; N, 4.9. $C_{12}H_{10}Cl_2NOP$ requires: C, 50.4; H, 3.5; N, 4.9%).

Diphenylphosphinic N-*methoxyamide.* An ether soln of free methoxyamine (0.29M) was prepared by adding methoxyamine hydrochloride (1.0 g) to 60% KOHaq (2 ml) in the presence of ether (20 ml) and warming so that the liberated methoxyamine codistilled with the ether (b.p. 34–36°).[31] The soln was dried (Na_2SO_4 then $CaSO_4$) and standardised by taking a portion (1 ml), passing in HCl, and weighing the precipitated hydrochloride. Diphenylphosphinic chloride (0.14 g, 0.59 mmol) in ether was added dropwise to methoxyamine (1.5 mmol) in ether. Volatile material was evaporated and the residue was extracted with CH_2Cl_2. The extract was washed with $NaHCO_3$aq, dried, and concentrated. Crystallisation from EtOAc afforded *diphenylphosphinic* N-*methoxyamide* (0.08 g, 0.32 mmol, 54%), m.p. 173–175°C, *m/e* 247 (M^+, 3), 216 (M^+–OMe, 100), 201 (M^+–NHOMe, 40), and 199 (85%), ν_{max} (Nujol) 3150 (NH) and 1210 cm^{-1} (P=O), $\delta(CDCl_3)$ 8.0–7.15 (10H, m), 6.30 br (1H), and 3.50 (3H, s) (Found: C, 62.9; H, 5.6; N, 5.6. $C_{13}H_{14}NO_2P$ requires: C, 63.2; H, 5.7; N, 5.7%).

Photochemical reactions. These employed a 125-W medium pressure mercury lamp in a water-cooled quartz envelope immersed in the stirred mixture. The vessel was sometimes cooled externally with ice. Reactions of azides were monitored by means of a gas burette connected to the vessel, and irradiation was continued until evolution of N_2 ceased. In general the mixture was examined by glc (3% silicone OV 17) and, after evaporation of solvent, by ^1H NMR. The crude product was then chromatographed on a column of alumina, eluting with ether containing an increasing proportion (0–10%) of MeOH. The fractions were examined by glc and/or NMR and combined as appropriate. Products were isolated by Kugelrohr distillation and/or crystallisation. They were identified as detailed below or (where no details are given) by comparison with the authentic samples prepared above. Yields generally refer to material after chromatographic separation but before final purification. Control dark reactions showed that in MeOH the phosphinic azides suffered extensive solvolysis to the methyl phosphinates.

Diphenylphosphinic azide in methanol. The azide (1.21 g, 5.0 mmol) on irradiation in MeOH (60 ml) at 7° for 6 hr gave methyl diphenylphosphinate (0.094 g, 8%), methyl NP-diphenylphosphonamidate (0.50 g, 41%), crystallised from EtOAc, m.p. 122–124° (lit,[32] 123.5–125°), ν_{max} (Nujol) 3160 (NH), 1215 (P=O), and 1050 cm^{-1} (POMe), $\delta(CDCl_3)$ 7.95–7.2 (6H, m, PPh and NH), 7.1–6.6 (5H, m, NPh), and 3.73 (3H, d, J_{PH} 11 Hz), diphenylphosphinic N-methoxyamide (0.030 g, 2.4%), and diphenylphosphinic amide (0.19 g, 18%). These products corresponded to glc peaks of t_R 3.7, 6.0, and 8.2 min (two unresolved peaks) at 244° in the crude reaction mixture.

Di-p-tolylphosphinic azide in methanol. The azide (1.03 g, 3.8 mmol) on irradiation in MeOH (60 ml) at 10° for 4 hr gave methyl di-*p*-tolylphosphinate (0.33 g, 33%), *methyl* NP-*di-p-tolylphosphonamidate* (0.45 g, 43%, crude), crystallised form EtOAc-petroleum (1:1), m.p. 101–103°, *m/e* 275 (M^+, 18), 169 ($M^+ - NHAr$, 14), and 94 (100), ν_{max} (Nujol) 3170 (NH), 1220 (P=O), and 1050 cm^{-1} (POMe), $\delta(CDCl_3)$ 7.83 (2H, dd, J_{PH} 13, J_{HH} 8 Hz), 7.30 (2H, dd, J_{PH} 4, J_{HH} 8 Hz), 7.00 (4H, approx. s), 6.63 br (1H, d, J_{PH} 6 Hz), 3.88 (3H, d, J_{PH} 11 Hz), 2.38 (3H, s), and 2.23 (3H, s) (Found: C, 65.5; H, 6.6; N, 5.1. $C_{15}H_{18}NO_2P$ requires: C, 65.4; H, 6.6; N, 5.1%), and di-*p*-tolylphosphinic amide (0.24 g, 26%). These products corresponded to glc peaks of t_R 6.5, 9.9, and 14.6 min at 250°. A minor chromatography fraction contained a compound also having t_R 14.6 min and an NMR spectrum (including δ3.55, s) consistent with it being (impure) di-*p*-tolylphosphinic N-methoxyamide (*ca* 1%) but the structure was not firmly established.

Di-p-anisylphosphinic azide in methanol. The azide (0.50 g, 1.65 mmol) on irradiation in MeOH (60 ml) at 10° for 3.3 hr gave methyl di-*p*-anisylphosphinate (0.017 g, 3.5%), *methyl* NP-*di-p-anisylphosphonamidate* (0.27 g, 53%), b.p. 140° (oven temp) at 0.005 mmHg, crystallised from ether, m.p. 90.5–95°, *m/e* 307 (M^+, 85) and 185 (M^+–NHAr, 100%), ν_{max} (Nujol) 3140 (NH), 1210 (P=O), and 1030 cm^{-1} (POMe), $\delta(CDCl_3)$ 7.82 (2H, dd, J_{PH} 13, J_{HH} 8 Hz), 7.15–6.8 (7H, m, includes NH), 3.82 (3H, d, J_{PH} 11 Hz), 3.82 (3H, s), and 3.72 (3H, s) (Found: C, 58.0; H, 5.8; N, 4.5. $C_{15}H_{18}NO_4P$ requires: C, 58.6; H, 5.9; N, 4.6%), and di-*p*-anisylphosphinic amide (0.19 g, 42%). These products cor-

responded to glc peaks of t_r 6.8, 8.7, and 12.8 min at 284° in the crude mixture.

Di(p-chlorophenyl)phosphinic azide in methanol. The azide (0.47 g, 1.5 mmol) on irradiation in MeOH (60 ml) at 10° for 3 hr gave methyl di(*p*-chlorophenyl)phosphinate (0.15 g, 33%) and a non-crystalline mixture of methyl N-phenyl-P-*p*-chlorophenylphosphonamidate (major component by glc) and methyl NP-di(*p*-chlorophenyl)phosphonamidate (0.22 g, *ca* 49% total), b.p. 140° (oven temp) at 0.05 mmHg, *m/e* 315, 317 and 319 (9), 281 and 283 (100), 189 and 191 (53), and 111 and 113 (34%), ν_{max} (film) 3150 (NH), 1215 (P=O), and 1030 cm^{-1} (POMe), $\delta(CDCl_3)$ 7.78 (2H, dd, J_{PH} 13, J_{HH} 8 Hz), 7.6–6.7 (*ca* 7.5 H; includes large peak at 6.97; assumed to include NH), and 3.84 (3H, d, J_{PH} 12 Hz) (Found: C, 53.7; H, 4.7; N, 4.5%). These products corresponded to glc peaks of t_R 4.85, 5.1 (shoulder), and 8.5 min at 285° in the crude mixture. Di(*p*-chlorophenyl)phosphinic amide was not isolated nor was it detected by glc (t_R 11.4 min for the authentic sample). The composition of the mixture of methyl phosphonamidates was confirmed by degradation with anhyd HCl in warm MeOH; after neutralisation of the soln with ammonia, glc at 130° showed the presence of both aniline (t_R 2.2 min) and *p*-chloroaniline (t_R 7.4 min), and at 196° showed dimethyl *p*-chlorophenylphosphonate (t_R 4.7 min) to be present but dimethyl phenylphosphonate (t_R 3.0 min) to be absent.

Methyl N-p-chlorophenyl-P-phenylphosphonamidate in methanol. The phosphonamidate (60 mg) in MeOH (60 ml) (containing 10 mg methyl diphenylphosphinate as standard for glc analysis) was irradiated at room temp. Samples were removed at intervals of 0.5 hr and analysed by glc. The peak due to starting material (t_R 10.8 min at 250°) was gradually replaced by peaks due to methyl NP-diphenylphosphonamidate (t_R 5.9 min at 250°) and dimethyl phenylphosphonate (t_R 1.6 min at 210°) in the approx ratio 10:1. After 5 hr methyl NP-diphenylphosphonamidate was isolated (tlc) and its identity confirmed by comparison with the sample obtained in a previous experiment.

Dimethyl N-p-chlorophenylphosphoramidate in methanol. The phosphoramidate (115 mg) in MeOH (65 ml) was irradiated for 1.3 hr. Glc showed complete consumption of starting material (t_R 7.4 min at 200°) and formation of dimethyl N-phenylphosphoramidate (t_R 3.6 min at 200°); trimethyl phosphate (t_R 1.9 min at 140°) was not formed. The product was isolated by evaporation of the solvent and extraction of the residue with hot ether-petroleum (1:3) and shown to be identical with an authentic sample of dimethyl N-phenylphosphoramidate.

Trimethylammonium-N-diphenylphosphinylimine in dimethyl sulphoxide.[9] The ylid (1.00 g, 3.7 mmol) in DMSO (60 ml) was irradiated at 20° for 7.5 hr. Chromatography afforded N-diphenylphosphinyldimethylsulphoximine (0.30 g, 28%) and diphenylphosphinic amide (0.38 g, 47%), t_R 26.4 and 8.1 min respectively at 245°. The identity of the sulphoximine was established by comparison with the product obtained by heating trimethylammonium-N-diphenylphosphinylimine (1.0 g, 3.6 mmol) in dry DMSO (20 ml) at *ca* 185° for 5 hr. Evaporation of the excess DMSO followed by chromatography on alumina gave, by elution with ether containing 3–4% methanol, N-diphenylphosphinyldimethylsulphoximine (0.13 g, 0.45 mmol, 12%), m.p. 164–165.5° (from toluene) (lit,[9] 168–168.5°), *m/e* 293 (M^+, 55), 292 (60), 278 (M^+–Me, 70), and 216 (100%), ν_{max} (Nujol) 1220, 1190, and 1160 cm^{-1}, $\delta(CDCl_3)$ 8.2–7.3 (10H, m) and 3.28 (6H, s).

Diphenylphosphinic azide in dimethyl sulphoxide. A soln of the azide (1.00 g, 4.1 mmol) in anhyd DMSO (60 ml) was irradiated for 7.3 hr at room temp, when IR showed the absence of unchanged azide. The solvent was evaporated under reduced pressure and CH_2Cl_2 (25 ml) was added to the residue. Some insoluble material (0.20 g) was filtered off and identified as diphenylphosphinic acid. The soln was treated with an excess of diazomethane, concentrated, and chromatographed on alumina. Elution with ether containing 3–8% MeOH gave methyl diphenylphosphinate (0.56 g) (derived from diphenylphosphinic acid; the total yield of acid was therefore 82%), N-diphenylphosphinyldimethylsulphoximine (0.034 g, 2.8%), and diphenylphosphinic amide (0.042 g, 4.7%). These products accounted for glc peaks of t_R 3.4, 25.6, and 7.2 min at 245° in the diazomethane-treated mixture; a fourth product having t_R similar to that of the phosphinic amide was not isolated.

Trimethylammonium-N-diphenylphosphinylimine in methanol. The ylid (1.00 g, 3.7 mmol) in MeOH (60 ml) was irradiated at 15° for 24 hr. For the crude product, glc at 245° showed only diphenylphosphinic amide (t_R 8.1 min) in substantial amount, with very small peaks of t_R 3.6 and 5.2 min but no methyl NP-diphenylphosphonamidate (t_R 5.8 min; < 1% yield), and ^1H NMR showed no signals at δ7.1–6.5 (NPh) or 4.0–3.5 (OMe). Chromatography afforded only the phosphinic amide (0.34 g, 43%).

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