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PHOTOLYSIS OF SOME UNSYMMETRICAL PHOSPHINIC AZIDES IN METHANOL

RELATIVE MIGRATORY APTITUDES OF ALKYL GROUPS AND PHENYL IN THE CURTIUS-LIKE REARRANGEMENT

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Abstract—When an alkylphenylphosphinic azide $RPhP(O)N_3$ (R = Me, Et, Pr^i, or Bu^t) is photolysed in MeOH either the alkyl or phenyl group can migrate from P to N in the Curtius-like rearrangement. The composition of the product shows that migration of the alkyl group R is preferred. However, the preference is not great and decreases as R changes $Bu^t \rightarrow Pr^i \rightarrow Et \rightarrow Me$ (approx. migratory aptitudes relative to Ph: 2.1, 1.7, 1.3 and 1.2 respectively), probably because the Ph–P bond is better able to assume the correct conformation for Ph migration when R is less bulky. For t-butylmethylphosphinic azide there is very little preference for migration of Bu^t relative to Me. Small amounts of unrearranged products such as $Bu^tPhP(O)NHOMe$ and $Bu^tPhP(O)NH_2$ are generally produced in the photolyses, together with the methyl phosphinates RPhP(O)OMe (major product when R = Me) resulting from (non-photochemical) solvolysis of the azide.

Both dialkyl and diaryl phosphinic azides (**1**, R = alkyl or aryl) decompose with loss of N_2 on photolysis in protic solvents.[1,2] In methanol the major product is the methyl phosphonamidate **3** resulting from Curtius-like rearrangement and reaction of the resulting monomeric metaphosphonimidate **2** with the solvent. Notable minor products are those derived (formally) from phosphinyl nitrenes reacting with the solvent by insertion or abstraction. Nitrenes may also be intermediates in the Curtius rearrangement; alternatively, the azides may decompose with concerted elimination of N_2 and migration of the group R. For acyl azides ($RCON_3$) it is now reasonably certain that the thermal Curtius rearrangement proceeds by a concerted mechanism,[3] and even in the photochemical reactions, where a part of the azide undoubtedly decomposes to a nitrene, much evidence suggests that this nitrene plays no part in the Curtius rearrangement.[3,4] Nonetheless, it cannot be assumed that phosphinic azides also rearrange by a concerted mechanism. In particular, whereas acyl azides are essentially planar, phosphinic azides (**1**) are tetrahedral, with the migrating group R lying outside the plane defined by the P=O group and the N atom to which it migrates. In the hope of gaining some evidence as to the mechanism of the Curtius-like rearrangement we have extended our investigation of phosphinic azides to include some unsymmetrical compounds.

RESULTS AND DISCUSSION

Methylphenylphosphinic azide (**5**, R = Me) has been reported by Baldwin *et al.*,[5] and other alkylphenylphosphinic azides **5** having R = Et, Pr^i, and Bu^t were readily obtained from the appropriate phosphinic chlorides [RPhP(O)Cl] and sodium azide. By using acetonitrile as solvent even the sterically hindered t-butylphenylphosphinic chloride was completely converted into the azide after 27 hr at room temperature.

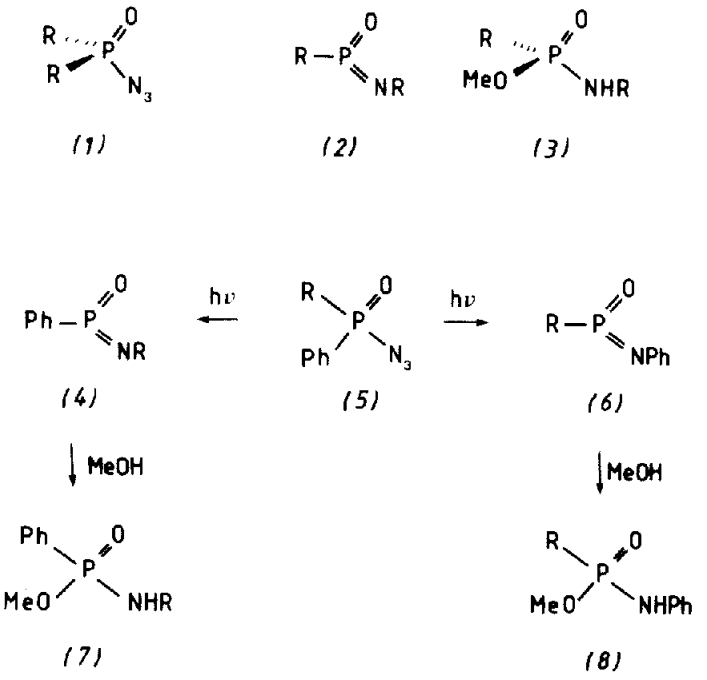
On irradiation in methanol solvolysis of the azides competed with their N_2-eliminating decomposition. The yield of the methyl phosphinate [RPhP(O)OMe] isolated by chromatography was minimal (*ca* 1%) in the case of t-butylphenylphosphinic azide but increased markedly as the bulk of the P-alkyl group decreased: R = Pr^i, 4%; R = Et, 15%; R = Me, 51% (*ca* 75% by NMR analysis of the crude mixture). Control (dark) experiments showed that this solvolysis could be accounted for largely, and perhaps entirely, by non-photochemical reaction of the azide in its ground state.

The principal products of photochemical decomposition were the methyl phosphonamidates resulting from Curtius-like rearrangement (Table 1). The important difference between the present reactions and those studied previously is that here the azides, being unsymmetrical, can rearrange in two distinct ways: either the alkyl group or the phenyl group can migrate from P to N (Scheme). This possibility makes phosphinic azides particularly interesting as both acyl and sulphonyl azides ($RCON_3$ or RSO_2N_3) can rearrange in only one way. For each azide **5** the methyl phosphonamidate isolated by chromatography was a mixture of the two possible isomers **7** and **8**. Separation of the isomers was accomplished by fractional crystallisation for R = Bu^t and by preparative GLC for R = Pr^i. In other cases the individual components of the mixture were not isolated but their identities were firmly established by comparison with authentic samples prepared as shown in eqns (1) and (2).

$$PhP(O)Cl_2 \xrightarrow{MeOH} PhP(O)(Cl)OMe \xrightarrow{RNH_2} \mathbf{7} \quad (1)$$

$$RP(O)Cl_2 \xrightarrow{MeOH} RP(O)(Cl)OMe \xrightarrow{PhNH_2} \mathbf{8} \quad (2)$$

Our particular concern was with the migratory aptitudes of the alkyl groups relative to phenyl in the Curtius rearrangements. Provided that the monomeric metaphosphonimidates **4** and **6** are trapped quantitatively by the solvent, these migratory aptitudes will be reflected in the ratios of the isomeric methyl phosphonamidates **7** and **8**. Because the N-alkyl compounds **7** were found to be susceptible to hydrolysis and might have decomposed



Scheme.

Table 1. Methyl phosphonamidates 7 and 8 from photolysis of alkylphenylphosphinic azides in methanol

Azide	Yield (%)[a] 7 + 8	Ratio NMR	7 : 8 GLC
5(R=Me)	14 (56)	1.2:1	
5(R=Et)	41 (50)	1.3:1	1.25:1
5(R=Pr^i)	42 (44)	~1.7:1	1.7:1
5(R=Bu^t)	54 (61)	2.1:1	2.1:1

[a] Isolated yields of the mixture of 7 and 8. Yields shown in parentheses have been corrected for unchanged azide and azide consumed by solvolysis; they are therefore based on the amount of azide undergoing N_2-eliminating decomposition.

to some extent during chromatography, the phosphonamidate ratios were generally determined by examination of the crude reaction products. The values shown in Table 1 were obtained by ^{1}H NMR spectroscopy (comparison of the P–OMe signals), and also by GLC (assuming equal detector response for the two isomers) where satisfactory separation could be achieved.

If these ratios are to be a true measure of the migratory aptitudes it is essential that the phosphonamidates once formed do not suffer photochemical degradation. To minimise the risk of degradation irradiation was continued only as long as an appreciable amount of azide remained, i.e. only as long as N_2 was being evolved at an appreciable rate. In addition, a more detailed examination was made of t-butylphenylphosphinic azide, this being the azide that required the longest period of irradiation and also the one that gave the lowest proportion of the N-phenyl phosphonamidate. GLC analysis revealed that during photolysis (using a more dilute solution than in the preparative experiment) the phosphonamidate ratio increased from 1.95:1 (in favour of the N-t-Bu isomer) after 0.8 hr, when 70% of the azide had reacted, to 2.1:1 after 2.3 hr, when practically all the azide had been consumed. Irradiation for a further 2 hr caused a noticeable decrease in the amount of the N-phenyl phosphonamidate and a consequent increase in the phosphonamidate ratio to 2.5:1. Likewise with ethylphenylphosphinic azide, prolonged irradiation of the photolysis products caused some degradation of the N-phenyl phosphonamidate although in this case the phosphonamidate ratio changed comparatively slowly. Thus the phosphonamidate ratios shown in Table 1 may slightly understate the proportion of the N-phenyl isomer actually formed, but any discrepancies will be small and the trends revealed are undoubtedly real.

It had been hoped that by examining migratory aptitudes we would obtain evidence as to the mechanism of the Curtius-like rearrangement of phosphinic azides. On the one hand a lack of discrimination between different

migrating groups would accord with the formation of a high energy nitrene intermediate which subsequently rearranges to metaphosphonimidate via an early transition state. On the other hand, strong discrimination would suggest that migration is well advanced in the rearrangement transition state, as it might well be if the rearrangement proceeds directly from the azide and is concerted with the loss of N_2.

Our results (Table 1) show that there is a small preference for migration of alkyl relative to phenyl, and that this preference becomes more marked as the alkyl group changes $Me \rightarrow Et \rightarrow Pr^i \rightarrow Bu^t$. However, the discrimination between migrating groups is remarkably small and may simply be a consequence of conformational factors. Assuming that migration of the phenyl group involves the aromatic π electron system in the initial bonding to N (Fig. 1; shown for a nitrene but the

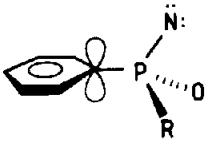


Fig. 1.

situation will be essentially the same for rearrangement of the azide), the conformation about the Ph–P bond must be such as to place the p-orbital axis in the same plane as the P–N bond. In this conformation the Ph group is liable to steric interaction with the alkyl group R. The more bulky the alkyl group, the less favourable will be the conformation required for phenyl migration. The greater preference for alkyl migration (relative to phenyl) as R changes $Me \rightarrow Et \rightarrow Pr^i \rightarrow Bu^t$ may therefore be due to increasing hindrance of phenyl migration rather than to any increase in the intrinsic ability of the alkyl group to stabilise the rearrangement transition state.

To explore this possibility further we prepared the unsymmetrical dialkylphosphinic azide **9** since this allows direct comparison of Me and Bu^t as migrating groups. A mixture of the two possible methyl phosphonamidates (65% isolated) was obtained on photolysis in methanol, and its composition indicated only a marginal preference for migration of Bu^t relative to Me (1.2:1 by ^1H NMR; 1.05:1 by GLC). Thus while rearrangement is not entirely indiscriminate the preference for migration of Bu^t is so small as to be almost insignificant. In particular, it is less than would be expected from the migratory aptitudes of the individual alkyl groups relative to phenyl and as such adds credence to the ideas discussed above.

A noteworthy feature of the photolysis of azide **9** was the relatively high yield (14%) of the N-methoxyamide **10** formed by insertion of the singlet nitrene into the O–H bond of methanol. The alkylphenylphosphinic azides **5** resembled more closely the systems previously examined[1,2] with the insertion product being isolated in very low yield [3% for **5** ($R = Bu^t$)] or not at all. On the other hand azide **9** gave only 3% of the product **11** derived formally from the triplet nitrene by hydrogen abstraction whereas the azides **5** gave 7–13% of the corresponding phosphinic amides.†

As regards the involvement of nitrenes in the Curtius rearrangement of phosphinic azides, the picture remains unclear. The alternative concerted mechanism would proceed directly from the azide, but this would not be azide in its ground state. For photo-excited azide the thermal energy barrier to reaction is unlikely to be large[7] and the transition state for simultaneous migration and loss of N_2 might be rather insensitive to the nature of the migrating group.‡ Thus while the observed migratory aptitudes can be readily understood in terms of a nitrene intermediate they do not necessarily conflict with a concerted mechanism.

EXPERIMENTAL

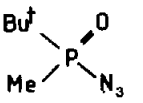
Instrumentation was as previously described.[9] Small scale distillations were carried out with a Kugelrohr apparatus and the stated b.p.s. are oven temps. Chromatography employed neutral alumina. GLC analyses were performed on a Pye 104 flame-ionisation chromatograph fitted with 1.5 m × 4 mm internal dia. 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. Petroleum refers to the fraction b.p. 60–80°.

Phosphinic chlorides. Methylphenylphosphinic chloride, b.p. 120–130° at 2–3 mmHg (lit.,[10] 105–110° at 0.05 mmHg), was prepared by a known method[10] and ethyl- and isopropyl-phenylphosphinic chlorides were obtained as previously described.[11] t-Butyl-methylphosphinic chloride, b.p. 118–120° at 32 mmHg, solidified when cool (lit.,[12] b.p. 99° at 10 mmHg, m.p. 37°), was prepared from methylphosphonous dichloride[13] by the method of Crofts and Parker[12] and t-butylphenylphosphinic chloride, b.p. 115–117° at 0.7 mmHg (lit.,[14] 100–104° at 2 mmHg) was similarly obtained from phenylphosphonous dichloride.

Phosphinic azides. The appropriate phosphinic chloride (8 mmol) and sodium azide (12 mmol) were stirred in dry acetonitrile (10 ml) at room temp for ≥ 16 hr. After filtration and evaporation of the solvent, Kugelrohr distillation afforded *t-butylphenylphosphinic azide* (85%), b.p. 114–119° (oven temp) at 0.1 mmHg, solidified when cool, $\delta(CCl_4)$ 8.0–7.3 (5H, m) and 1.13 (9H, d, J_{PH} 16 Hz) (Found: C, 53.7; H, 6.3; N, 18.9. $C_{10}H_{14}N_3OP$ requires C, 53.8; H, 6.3; N, 18.8%), using a reaction time of 27 hr; *isopropylphenylphosphinic azide* (78%), b.p. 135–140° (oven temp) at 0.1 mmHg, $\delta(CDCl_3)$ 8.1–73 (5H, m), 2.7–1.7 (1H, m), 1.25 (3H, dd, J_{PH} 19, J_{HH} 7 Hz and 1.13 (3H, dd, J_{PH} 19, J_{HH} 7 Hz) (Found: C, 51.4; H, 5.9; N, 20.0. $C_9H_{12}N_3OP$ requires: C, 51.7; H, 5.8; N, 20.1%); *ethylphenylphosphinic azide* (92%), b.p. 130–135° (oven

†No phosphinic amide was actually isolated in the case of **5** (R = Me) but as $MePhP(O)NH_2$ is sterically unhindered and extremely susceptible to hydrolysis (and methanolysis) [6] this does not necessarily mean that it was not formed.

‡Note, however, that substantial differences in migratory aptitude can be observed in photochemical rearrangements e.g. *p*-methoxy- and *p*-cyano-phenyl migrate 10–15 times as readily as phenyl in the photochemical rearrangement of 4,4-diarylcyclohexenones.[8]



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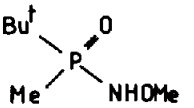

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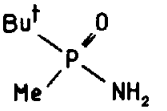

(11)

temp) at 0.1 mmHg, $\delta(CCl_4)$ 8.2–7.4 (5H, m), 1.97 (2H, approx. dq, J_{PH} 14, J_{HH} 7 Hz), and 1.15 (3H, dt, J_{PH} 20, J_{HH} 7 Hz) (Found: C, 48.6; H, 5.3; N, 21.25. $C_8H_{10}N_3OP$ requires: C, 49.2; H, 5.2; N, 21.5%); *methylphenylphosphinic azide* (74%), b.p. 123–128° (oven temp) at 0.2 mmHg (lit.,[5] 65° at 3×10^{-4} mmHg), $\delta(CDCl_3)$ 8.2–7.4 (5H, m) and 1.85 (3H, d, J_{PH} 14 Hz); and *t-butylmethylphosphinic azide* (83%), b.p. 90–95° (oven temp) at 0.6 mmHg, $\delta(CDCl_3)$ 1.58 (3H, d, J_{PH} 13 Hz) and 1.23 (9H, d, J_{PH} 17 Hz) (Found: C, 36.3; H, 7.7; N, 25.7. $C_5H_{12}N_3OP$ requires: C, 37.3; H, 7.5; N, 26.1; $C_5H_{12}N_3OP \cdot 0.2H_2O$ requires: C, 36.45; H, 7.6; N, 25.5%), using a reaction time of 22 hr. The IR spectra (liquid films) of these compounds all included strong absorptions at *ca* 2150 (N_3) and 1280–1205 cm^{-1} (2 or 3 peaks) (P=O).

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

Methyl N-*isopropyl*-P-*phenylphosphonamidate.* A soln of phenylphosphonic dichloride (1.00 g, 5.1 mmol) (prepared by sulphuryl chloride oxidation[15] of phenylphosphonous dichloride) in ether (3 ml) was stirred at room temp while a mixture of MeOH (0.16 g, 5.0 mmol) and Et_3N (0.52 g, 5.1 mmol) in ether (3 ml) was added dropwise. The ppt (Et_3NHCl) was removed by filtration and isopropylamine (0.80 g, 13.5 mmol) in ether (3 ml) was added dropwise to the filtrate; after dilution with more ether (10 ml) the mixture was filtered and concentrated. Vacuum distillation gave a product which was contaminated with dimethyl phenylphosphonate. It was chromatographed on alumina, eluting with ether containing 0–4% MeOH, to give *methyl* N-*isopropyl*-P-*phenylphosphonamidate* (0.79 g, 73%), b.p. 160° (oven temp) at 0.3 mmHg, *m/e* 213 (M^+, 1), 198 (M^+–CH_3, 100), and 155 (M^+–NHC_3H_7, 90%), ν_{max} (film) 3200 (NH) and 1215 cm^{-1} (P=O), $\delta(CDCl_3)$ 8.2–7.4 (5H, m), 3.76 (3H, d, J_{PH} 11 Hz), 3.6–2.8 (2H; NHCH), 1.10 (3H, d, J_{HH} 6 Hz), and 1.06 (3H, d, J_{HH} 6 Hz) (Found: C, 55.2; H, 7.35; N, 6.4. $C_{10}H_{16}NO_2P \cdot 0.25H_2O$ requires: C, 55.2; H, 7.6; N, 6.4%).

Methyl N-*ethyl*-P-*phenylphosphonamidate.* This was prepared and purified as above but with $EtNH_2$ in place of i-$PrNH_2$ (55% yield); it had b.p. 150–160° (oven temp) at 0.1 mmHg, *m/e* 199 (M^+, 10), 184 (M^+–CH_3, 45), and 155 (M^+–NHC_2H_5, 100%), ν_{max} (film) 3220 (NH) and 1210 cm^{-1} (P=O), $\delta(CCl_4)$ 8.1–7.3 (5H, m), 5.0 br (1H), 3.72 (3H, d, J_{PH} 11 Hz), 2.84 (2H, m), and 1.05 (3H, t, J_{HH} 7 Hz) (Found: C, 52.6; H, 7.2; N, 6.7. $C_9H_{14}NO_2P \cdot 0.35H_2O$ requires: C, 52.6; H, 7.2; N, 6.8%).

Methyl N-*methyl*-P-*phenylphosphonamidate.* This was prepared as above but with $MeNH_2$[16] in place of i-$PrNH_2$; chromatography was unnecessary as the initial distillate, b.p. 138–142° (oven temp) at 0.2 mmHg, solidified and could be purified by crystallisation from ether. The resulting *phosphonamidate* (39%) had m.p. 37–39.5°, ν_{max} (melt) 3230 (NH) and 1215 cm^{-1} (P=O), $\delta(CDCl_3)$ 8.0–7.2 (5H, m), 4.4 br (1H), 3.72 (3H, d, J_{PH} 11 Hz), and 2.52 (3H, dd, J_{PH} 12, J_{HH} 6 Hz; after shaking with D_2O, d, J_{PH} 12 Hz) (Found: C, 51.6; H, 6.3; N, 7.4. $C_8H_{12}NO_2P$ requires: C, 51.9; H, 6.5; N, 7.6%).

Methyl N-*phenyl*-P-*ethylphosphonamidate.* Ethylphosphonic dichloride[17] was treated with MeOH (1 mol. equiv) and Et_3N and then with aniline (2.05 mol. equiv.) in essentially the same way as described above. After concentration, the crude product was dissolved in CH_2Cl_2, washed with water containing a little HCl, and distilled to give the *phosphonamidate* (55%), b.p. 175–180° (oven temp) at 0.2 mmHg, m.p. 71–72° from petroleum, *m/e* 199 (M^+, 55) and 93 ($PhNH_2^+$, 100%), ν_{max} (Nujol) 3140, 3085 (NH), and 1210 cm^{-1} (P=O), $\delta(CDCl_3)$ 7.4–6.9 (5H, m), 6.6 br (1H), 3.73 (3H, d, J_{PH} 11 Hz), 1.92 (2H, approx. dq, J_{PH} 17, J_{HH} 8 Hz), and 1.16 (3H, dt, J_{PH} 20, J_{HH} 8 Hz) (Found: C, 54.1; H, 7.1; N, 7.0. $C_9H_{14}NO_2P$ requires: C, 54.3; H, 7.1; N, 7.0%).

Methyl N-*phenyl*-P-*methylphosphonamidate.* A soln of methyl methylphosphonochloridate (1.25 g, 9.7 mmol), prepared from dimethyl methylphosphonate and oxalyl chloride,[18] in CH_2Cl_2 was added dropwise to a stirred soln of aniline (3.6 g, 39 mmol) in CH_2Cl_2 at 0°. After a further 2 hr at room temp the mixture was washed with water and dried (Na_2SO_4). Volatile material was removed under vacuum and the residue was crystallised from toluene to give methyl N-phenyl-P-methylphosphonamidate (0.79 g, 44%), m.p. 76–77° (lit.,[19] 76.5–77.5°C), ν_{max} (Nujol) 3160, 3085 (NH), and 1215 cm^{-1} (P=O), $\delta(CDCl_3)$ 7.5–6.9 (5H, m), 6.2 br (1H), 3.70 (3H, d, J_{PH} 11 Hz), and 1.62 (3H, d, J_{PH} 17 Hz).

Methyl N-*t-butyl*-P-*methylphosphonamidate.* t-$BuNH_2$ (3.6 g, 0.050 mol) in ether was added dropwise with stirring to an ice-cold soln of methyl methylphosphonochloridate (2.7 g, 0.021 mol) in ether. The mixture was allowed to warm to room temp and was then filtered and concentrated. Distillation of the residue (oven temp 100–110° at 0.8 mmHg) gave a solid which was crystallised from petroleum (b.p. 40–60°) to give *methyl* N-*t-butyl*-P-*methylphosphonamidate*, m.p. 58–62° (softened at 52°), ν_{max} (Nujol) 3180 (NH) and 1190 cm^{-1} (P=O), $\delta(CDCl_3)$ 3.64 (3H, d, J_{PH} 11 Hz), 2.6 br (1H), 1.48 (3H, d, J_{PH} 17 Hz), and 1.32 (9H, s) (Found: C, 43.05; H, 9.6; N, 8.25. $C_6H_{16}NO_2P$ requires: C, 43.6; H, 9.8; N, 8.5%).

Methyl N-*methyl*-P-*t-butylphosphonamidate.* A soln of benzyltrimethylammonium methoxide (1.45 g, 8.0 mmol) in MeOH (4 ml) was added dropwise to a stirred soln of t-butylphosphonic dichloride[17,20] (1.28 g, 7.3 mmol) in benzene. $MeNH_2$[16] (0.46 g, 15.0 mmol) in ether was then slowly added. The mixture was filtered and the filtrate was washed with water, dried, and distilled to give *methyl* N-*methyl*-P-*t-butylphosphonamidate* (0.54 g, 41%), b.p. 128–134° (oven temp) at 1 mmHg, solidified on cooling, ν_{max} (melt) 3170 (NH), 1200, and 1180 cm^{-1} (P=O), $\delta(CDCl_3)$ 3.68 (3H, d, J_{PH} 11 Hz), 2.75 (3H, dd, J_{PH} 10, J_{HH} 4 Hz), *ca* 2.4 br (1H), and 1.18 (9H, d, J_{PH} 16 Hz) (Found: C, 44.1; H, 9.6; N, 8.2. $C_6H_{16}NO_2P$ requires: C, 43.6; H, 9.8; N, 8.5%).

Phosphinic amides. *t*-Butylmethylphosphinic chloride in CH_2Cl_2 was allowed to react with an excess of ammonia for 18 hr. The mixture was filtered and the filtrate was evaporated. The residue was crystallised from toluene to give (impure) *t-butylmethylphosphinic amide* (70%), m.p. 110–113° (softens at 100°), *m/e* 135 (M^+, 25) and 79 (M^+–C_4H_8, 100%), ν_{max} (Nujol) 3250, 3130 (NH), and 1135 cm^{-1} (P=O), $\delta(CDCl_3)$ 2.7 br (2H), 1.40 (3H, d, J_{PH} 13 Hz), and 1.15 (9H, d, J_{PH} 16 Hz). Further purification by chromatography, sublimation, and repeated crystallisation raised the m.p. to 114–116° but produced no change in the spectra and failed to give a sample for which satisfactory elemental analysis could be obtained (Found: C, 41.2; H, 9.4; N, 10.5. $C_5H_{14}NOP$ requires: C, 44.4; H, 10.4; N, 10.4%). Other phosphinic amides were as previously described.[6,11]

Methyl phosphinates. Samples of all the required esters were available from other work.[21]

Photochemical reactions of phosphinic azides. A 125-W medium pressure mercury lamp in a water-cooled quartz envelope was immersed in a stirred soln of the azide (6 mmol) in MeOH (60 ml) at 10–15°. Irradiation was continued until evolution of N_2 became very slow or ceased. The mixture was examined by GLC and, after evaporation of the solvent, by NMR. A measured portion (*ca* 80%) of the crude product was then chromatographed on alumina, eluting with ether containing an increasing proportion of MeOH (0–8%). The fractions were examined by GLC and/or NMR and combined as appropriate. In the following accounts the products are reported in the order in which they were eluted, although in general none of the fractions containing the methyl phosphonamidates consisted entirely of one isomer. The products were isolated by Kugelrohr distillation and/or crystallisation and in most cases (where no details are given) were identified by comparison with authentic samples. Yields generally refer to material after chromatographic separation but before final purification. Wherever possible the ratio of the isomeric methyl phosphonamidates was determined by analysis (GLC and NMR) of the crude product so as to avoid any errors due to possible slight decomposition during chromatography.

Control (dark) reactions showed that in MeOH in the absence of light the azides formed only the corresponding methyl phosphinates; during the time employed for the photochemical reactions this non-photochemical solvolysis was negligible (< 1% by GLC) for the t-butylphenyl and t-butylmethyl azides, slight (*ca* 2% by GLC) for the isopropylphenyl azide, but substantial for the ethylphenyl ($t_{0.5}$ *ca* 8 hr by NMR) and methylphenyl ($t_{0.5}$ *ca* 2.5 hr by ^{31}P NMR) phosphinic azides.

t-Butylphenylphosphinic azide. Irradiation in MeOH for 17.5 hr gave unreacted azide (2% isolated: *ca* 10% by GLC); a

mixture of two compounds (54% total) which on fractional crystallisation afforded *methyl* N-*t-butyl*-P-*phenylphosphonamidate*, m.p. 88–90° from petroleum, *m/e* 227 (M^+, 4), 212 (M^+–CH_3, 100), 180 (19), and 155 (M^+–NHC_4H_9, 60%), ν_{max} (Nujol) 3170 (NH) and 1240–1200 cm^{-1} (several maxima, P=O), $\delta(CDCl_3)$ 8.05–7.3 (5H, m), 3.67 (3H, d, J_{PH} 11 Hz), 2.7 br (1H), and 1.27 (9H, s) (Found: C, 58.2; H, 8.0; N, 6.2. $C_{11}H_{18}NO_2P$ requires: C, 58.1; H, 8.0; N, 6.2%), and *methyl* N-*phenyl*-P-*t-butylphosphonamidate*, m.p. 186–188°C from ethyl acetate, *m/e* 227 (M^+, 100) and 93 ($PhNH_2^+$, 100%), ν_{max} (Nujol) 3140, 3080 (NH), 1230, and 1200 cm^{-1} (P=O), $\delta(CDCl_3)$ 7.15 (5H, approx. s), 5.0 br (1H, s), 3.80 (3H, d, J_{PH} 11 Hz), and 1.20 (9H, d, J_{PH} 17 Hz) (Found: C, 58.3; H, 8.0; N, 6.3. $C_{11}H_{18}NO_2P$ requires: C, 58.1; H, 8.0; N, 6.2%), t_R 5.4 and 7.1 min respectively (3% OV 17 at 186°; the azide also has t_R 5.4 min); *t-butylphenylphosphinic* N-*methoxyamide* (*ca* 3%), sublimed at 100° at 0.05 mmHg, m.p. 164–167° (softens at 154°) from ethyl acetate-petroleum, *m/e* 227 (M^+, 12), 181 (M^+–NHOMe, 9), 141 (70), 140 (60), and 125 (M^+–NHOMe–C_4H_8, 100%), ν_{max} (Nujol) 3090 (NH) and 1170 cm^{-1} (P=O), $\delta(CDCl_3)$ 8.2–7.4 (5H, m), 6.55 br (1H), 3.75 (3H, s), and 1.22 (9H, d, J_{PH} 15 Hz) (insufficient pure material obtained for elemental analysis); and t-butylphenylphosphinic amide (7%). A very small amount of methyl t-butylphenylphosphinate (*ca* 1%) was detected by GLC but was not isolated. The ratio of phosphonamidates was 2.1:1 by NMR (POMe signals; major isomer at higher field in $CDCl_3$) in favour of methyl N-t-butyl-P-phenylphosphonamidate.

The experiment was repeated using a more dilute soln in a Rayonet reactor fitted with 254 nm lamps. Samples were withdrawn at intervals and examined by GLC (3% OV 225 at 190°). Under these conditions the azide (t_R 3.3 min) was *ca* 97% consumed after 2.3 hr when the ratio of the N-t-butyl and N-phenyl phosphonamidates (t_R 3.9 and 6.2 min respectively) was 2.1:1 (uncalibrated peak areas). After 0.8 hr this ratio was 1.95:1 (and *ca* 30% of the azide remained); after 4.3 hr it was 2.5:1 as a result of partial decomposition of the N-phenyl compound.

Isopropylphenylphosphinic azide. Irradiation in MeOH for 14.5 hr gave methyl isopropylphenylphosphinate (4%); a mixture of two phosphonamidates (42% total) which by preparative GLC (10% OV 17 at 218°) afforded methyl N-isopropyl-P-phenylphosphonamidate, b.p. 120–130° (oven temp) at 0.04 mmHg, spectra as for the authentic sample, and *methyl* N-*phenyl*-P-*isopropylphosphonamidate*, m.p. 115–117° from petroleum, *m/e* 213 (M^+, 100) and 93 ($PhNH_2^+$, 100%), ν_{max} (Nujol) 3130, 3080 (NH), and 1210 cm^{-1} (P=O), $\delta(CDCl_3)$ 7.45–6.8 (5H, m), 6.75 br (1H), 3.77 (3H, d, J_{PH} 11 Hz), 2.55–1.8 (1H, m), 1.27 (3H, dd, J_{PH} 18, J_{HH} 7 Hz), and 1.13 (3H, dd, J_{PH} 18, J_{HH} 7 Hz) (Found: C, 56.4; H, 7.5; N, 6.6. $C_{10}H_{16}NO_2P$ requires: C, 56.3; H, 7.6; N, 6.6%), t_R 5.6 and 7.3 min respectively (3% OV 17 at 194°); and isopropylphenylphosphinic amide (13%). The ratio of the phosphonamidates was 1.7:1 by GLC (uncalibrated peak areas) and approximately the same by ^1H NMR (POMe signals; major isomer at lower field in benzene; not resolved in $CDCl_3$) where the presence of methyl isopropylphenylphosphinate precluded accurate measurement. The GLC detector was calibrated using a chromatography fraction containing only the two phosphonamidates in a ratio measured accurately by NMR (in benzene); this showed that the response was the same (±9%) for the two isomers.

Ethylphenylphosphinic azide. Irradiation in MeOH for 7 hr gave methyl ethylphenylphosphinate (15%; *ca* 18% by NMR); a mixture of two phosphonamidates (41% total) which were not separated but were characterised by comparison with authentic samples as methyl N-ethyl-P-phenylphosphonamidate and methyl N-phenyl-P-ethylphosphonamidate, t_R 8.1 and 9.4 min respectively (3% OV 17 at 190°)); and ethylphenylphosphinic amide (11%). The ratio of the phosphonamidates was 1.3:1 by ^1H NMR (POMe signals; major isomer at lower field in $CDCl_3$) and 1.25:1 by GLC (uncalibrated peak areas) in favour of methyl N-ethyl-P-phenylphosphonamidate. When the experiment was repeated using a more dilute soln the azide was largely consumed within 1 hr. On continued irradiation the phosphonamidate ratio of 1.3:1 (by GLC) had not changed appreciably after 2 hr but after 4 hr it had increased to 1.45 as a result of partial decomposition of the N-phenyl phosphonamidate.

Methylphenylphosphinic azide. Irradiation in MeOH for 4 hr gave predominantly methyl methylphenylphosphinate (51% isolated; *ca* 75% by NMR). One later chromatography fraction contained only methyl N-methyl-P-phenylphosphonamidate, identified by comparison with the authentic sample, and this was followed by a mixture of the same compound and methyl N-phenyl-P-methylphosphonamidate (14% total) which was also characterised by comparison with an authentic sample, t_R 7.0 min (3% OV 17 at 194°) for both phosphonamidates. A product (*ca* 3%) having the same t_R (10.4 min) as methylphenylphosphinic amide was detected but not isolated. The ratio of the isolated phosphonamidates was 1.2:1 by NMR (POMe signals; major isomer at lower field in $CDCl_3$; comparison of PMe and NMe signals gave 1.25:1) in favour of methyl N-methyl-P-phenylphosphonamidate; because the spectrum of the crude product was dominated by methyl methylphenylphosphinate it was not possible to measure the ratio of phosphonamidates accurately, but it was clear that it did not differ significantly from that of the isolated material.

t-Butylmethylphosphinic azide. Irradiation in MeOH for 5 hr gave a mixture of methyl N-t-butyl-P-methylphosphonamidate and methyl N-methyl-P-t-butylphosphonamidate (65% total), t_R 5.1 and 6.4 min respectively (3% OV 17 at 133°), which was not separated but was analysed by comparison with authentic samples, and *t-butylmethylphosphinic* N-*methoxyamide* (14%), b.p. 100–110° (oven temp) at 3 mmHg, *m/e* 165 (M^+, 15), 150 (M^+–Me, 8), 119 (M^+–NHOMe, 22), 109 (M^+–C_4H_8, 25), 79 (M^+–C_4H_8–CH_2O, 100), and 78 (80%), ν_{max} (film) 3110 (NH) and 1175 cm^{-1} (P=O), $\delta(CDCl_3)$ 3.63 (3H, s), 1.48 (3H, d, J_{PH} 12 Hz), and 1.19 (9H, d, J_{PH} 15 Hz) (Found: C, 43.4; H, 9.8; N, 8.3. $C_6H_{16}NO_2P$ requires: C, 43.6; H, 9.8; N, 8.5%). This had the same t_R (13.3 min) as an authentic sample of t-butylmethylphosphinic amide on 3% OV 17 at 133° but a shorter t_R (4.4 min) on 3% OV 210 at 148°; under the latter conditions the mixture was seen to contain a product (*ca* 3%) having the same t_R (5.1 min) as the authentic amide, but this was not isolated. A trace amount of methyl t-butylmethylphosphinate (< 1%) was also detected but not isolated. The ratio of the isolated phosphonamidates was 1.2:1 by NMR (comparing NMe and PBu^t or NBu^t and PMe signals) and 1.05:1 by GLC (uncalibrated peak areas) in favour of methyl N-t-butyl-P-methylphosphonamidate. For the crude product GLC gave a ratio of 1.15:1 but this was known to be exaggerated by the presence of a small amount of unchanged phosphinic azide (ν_{max} 2140 cm^{-1}) having the same t_R (5.1 min on 3% OV 17 at 133°) as the major phosphonamidate.

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