Photochemical Rearrangement of Dialkylphosphinic Azides in Methanol and Other Protic Solvents

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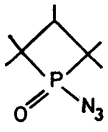
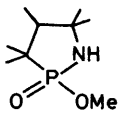
On photolysis in methanol di-t-butylphosphinic azide (4; R = Bu^t) rearranges with loss of nitrogen to give methyl *NP*-di-t-butylphosphonamidate (6; R = Bu^t, X = OMe) (71%), presumably by way of a monomeric metaphosphonimidate (5; R = Bu^t) which is trapped by the solvent. Analogous rearrangements occur in other alcohols and in t-butylamine, although di-t-butylphosphinic amide is also a substantial product in ethanol and the major product in isopropyl alcohol. Di-isopropylphosphinic azide (4; R = Pr^i) behaves in a similar way, but in methanol the less hindered diethylphosphinic azide (4; R = Et) suffers extensive solvolysis to methyl diethylphosphinate.

SOME time ago we reported the photochemical ring-expansion and ring-opening reactions of phosphetinic azides in methanol.[1] Thus, for example, the azide (1; N_3 *trans* to 3-Me group) afforded the cyclic phosphonamidate (2) (60%; mixture of *cis* and *trans* isomers) and the acyclic phosphonamidate (3) (16%). Westheimer and Wiseman [2] examined more closely the photolysis of (1)



(1)



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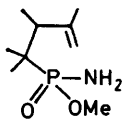


(3)

in methanol and established that the same mixture of the *cis* and *trans* isomers of (2) was obtained irrespective of the geometry of the starting azide. Their results are consistent with the intermediacy of a cyclic monomeric metaphosphonimidate, analogous to the isocyanate formed in the Curtius rearrangement [3] of an acyl azide.

The extent to which the behaviour of a phosphetinic azide is a consequence of its strained and rather rigid structure is not known, as hitherto no other investigations of the photolysis of phosphinic azides have been reported. We have now examined some simple acyclic dialkylphosphinic azides, looking particularly for Curtius-like rearrangements corresponding to the ring-expansion reactions of phosphetinic azides.

RESULTS AND DISCUSSION

Di-t-butylphosphinic azide (4; R = Bu^t), the acyclic analogue of (1), was prepared from the phosphinic chloride and sodium azide. Steric hindrance renders di-t-butylphosphinic chloride unreactive towards most nucleophiles, but it was completely converted into the azide within 4 h using a stirred suspension of sodium azide in dimethylformamide at 100 °C. (Pyridine was included in the reaction mixture as a potential catalyst but it probably played no part.) The related preparation of di-isopropylphosphinic azide (4; R = Pr^i) proceeded readily at room temperature. In the case of diethylphosphinic azide (4; R = Et), acetonitrile was used as solvent in place of dimethylformamide, as its lower b.p. simplifies its separation from the rather volatile product.

Solutions of the phosphinic azides (2.5—4.5 mmol) in various protic solvents (100 ml generally) were irradiated through quartz with a medium-pressure mercury-immersion lamp until evolution of nitrogen ceased. The Table shows the products isolated from each reaction, and their yields after chromatographic separation but before final purification.

Di-t-butylphosphinic azide in methanol gives mainly the phosphonamidate (6; R = Bu^t, X = OMe). This Curtius-like rearrangement corresponds to the ring-expansion reactions of phosphetinic azides. Di-isopropylphosphinic azide similarly gives the phosphonamidate (6; R = Pr^i, X = OMe) in methanol. In neither case did (non-photochemical) solvolytic displacement of azide compete significantly with nitrogen-eliminating photochemical decomposition. Control experiments showed that these two azides can be recovered completely unchanged after 17 h in methanol in the dark at room temperature. Diethylphosphinic azide, being more reactive (less sterically hindered) towards nucleophilic attack, is very largely solvolysed under the same conditions. It is therefore not surprising that photolysis of this azide in methanol afforded methyl *NP*-diethylphosphonamidate (6; R = Et, X = OMe) in much reduced yield (17% isolated; *ca.* 30% by n.m.r.) although the n.m.r. spectrum of the crude reaction mixture showed that it was the only important product other than the methyl diethylphosphinate resulting from solvolysis. By conducting the photolysis at low temper-

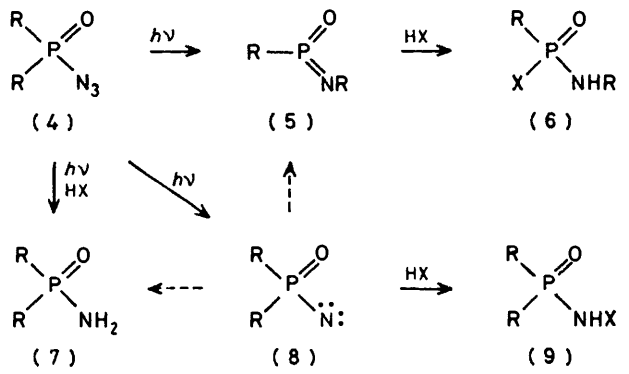
Photolysis of dialkylphosphinic azides in protic solvents [a]

Azide $R_2P(O)N_3$	Solvent XH	Yield (%) $RP(O)(X)NHR$	Yield (%) $R_2P(O)NH_2$	Other products
$Bu^t_2P(O)N_3$	MeOH	71	*b*	$Bu^t_2P(O)NHOMe$ (8%)
$Bu^t_2P(O)N_3$	EtOH	62	24	
$Bu^t_2P(O)N_3$	Pr^iOH	27	64	
$Bu^t_2P(O)N_3$	Bu^tOH	63	6.5	$Bu^t_2P(O)NHOBu^t$
$Bu^t_2P(O)N_3$	Bu^tNH_2	74	*b*	
$Pr^i_2P(O)N_3$	MeOH	71	5	$Pr^i_2P(O)NHOMe$
$Pr^i_2P(O)N_3$	EtOH	38	46	
$Pr^i_2P(O)N_3$	Pr^iOH	*b*	87	
$Pr^i_2P(O)N_3$	Bu^tNH_2	74	*b*	
$Et_2P(O)N_3$	MeOH	17 [c]	*b*	$Et_2P(O)OMe$ (48%) [c]

[a] Yields relate to isolated material after chromatographic separation but before final purification. [b] Not isolated but may have been formed in very low yield. [c] Substantial losses believed to have occurred during work-up and isolation.

atures (*ca.* −70 °C) it was possible to increase the phosphonamidate : phosphinate ratio to 2 : 1, but not to completely suppress solvolysis. It may be that some of the photo-excited azide reacts by solvolysis, and that this process is little influenced by reductions in temperature.

Some minor products, formed without rearrangement, were isolated from the photochemical reactions in methanol. Thus di-t-butylphosphinic azide gave the *N*-methoxyamide (9; R = Bu^t, X = OMe), while di-isopropylphosphinic azide gave not only an *N*-methoxy-compound but some di-isopropylphosphinic amide (7; R = Pr^i) (5%) as well.



SCHEME 1

When ethanol was used as solvent, the yield of the phosphonamidate (6; R = Bu^t or Pr^i, X = OEt) resulting from rearrangement was lower than in methanol, and that of the phosphinic amide (7; R = Bu^t or Pr^i) much higher. In isopropyl alcohol the corresponding amide became the major product (64%) from the photolysis of di-t-butylphosphinic amide and the only isolated product (87%) from the di-isopropyl azide; in both cases decomposition of the azide with elimination of nitrogen was several times faster than in methanol. Thus formation of the phosphinic amide assumes greater importance, relative to rearrangement, as the ease of abstraction of hydrogen from the alcohol solvent increases. Neither t-butyl alcohol nor t-butylamine possesses easily abstractable hydrogen atoms, and in these solvents the azides (4; R = Bu^t or Pr^i) gave high yields of the rearrangement products and little or no amide.

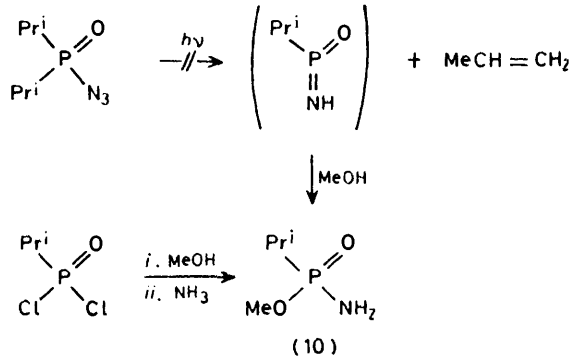
Lacking direct evidence, it is tempting to suppose that the phosphinic amide is derived from a triplet (either the triplet excited state of the azide or the triplet nitrene) and that rearrangement is a reaction of the singlet excited state or the singlet nitrene. Provided inter-system crossing by the singlet excited state of the azide competes efficiently with elimination of nitrogen, the course of the reaction will depend on the fate of the triplet excited state. If it reacts readily with the solvent (*e.g.* isopropyl alcohol) the photolysis product will be largely triplet-derived. If, on the other hand, it reacts slowly with the solvent (*e.g.* methanol) return to the ground state could be of major importance; in this case photochemical decomposition of the azide would be relatively inefficient, and could give largely singlet-derived products. Alternatively, the amide might be formed by a chain mechanism with induced decomposition of ground state azide [equations (1) and (2)]. The importance of

$$R_2P(O)N_3 + Me_2\dot{C}OH \longrightarrow R_2P(O)\dot{N}H + N_2 + Me_2CO \quad (1)$$

$$R_2P(O)\dot{N}H + Me_2CHOH \longrightarrow R_2P(O)NH_2 + Me_2\dot{C}OH \quad (2)$$

such a mechanism would obviously depend on the nature of the solvent. A similar mechanism has previously been considered by Reagan and Nickon [4] for the photochemical decomposition of methanesulphonyl azide in isopropyl alcohol.

The *N*-methoxyamides (9; R = Bu^t or Pr^i, X = OMe) resulting from photolysis of the azides in methanol [and also the tentatively identified (9; R = Bu^t, X = OBu^t) formed in t-butyl alcohol] are formally the products of insertion of a singlet nitrene (8) into the O–H bond of the solvent. It may be that singlet nitrenes are also precursors of the monomeric metaphosphonimidate intermediates (5) that lead to the rearrangement products, but it is equally possible that migration of the alkyl group from P to N is concerted with the loss of nitrogen from the excited azide. Whatever the detailed mechanism, it is clear that acyclic dialkylphosphinic azides share with phosphetinic azides the ability to undergo Curtius-like rearrangement on irradiation in protic solvents. On the other hand, they do not display reactions corresponding to the photochemical ring opening of phosphetinic azides. Such reactions would cause fragmentation, as shown in Scheme 2 for di-isopropyl-



SCHEME 2

phosphinic azide. However, we have found no evidence for methyl *P*-isopropylphosphonamidate (10) amongst the products of photolysis of di-isopropylphosphinic azide in methanol. By way of confirmation, an authentic sample of (10) was prepared (Scheme 2) and its absence from the photolysis reaction mixture proven by g.l.c. examination (1% would have been detected). For di-t-butylphosphinic azide there was likewise no evidence of fragmentation in methanol, although in this case confirmation was not possible as an authentic sample of methyl *P*-t-butylphosphonamidate was not available.

EXPERIMENTAL

Instrumentation was as previously described.[5] Methanol and ethanol were purified by distillation from their magnesium salts. Isopropyl alcohol was obtained free of peroxides by the method of Vogel.[6] t-Butylamine was refluxed over, and distilled from, potassium hydroxide pellets. Light petroleum refers to the fraction b.p. 60—80 °C unless otherwise indicated.

Phosphinic azides were assumed to be potentially explosive and toxic; appropriate precautions were taken although no difficulties were actually encountered.

Di-t-butylphosphinic Chloride.—Di-t-butylchlorophosphine[7] (3.3 g, 18.3 mmol) in dichloromethane (50 ml) was stirred vigorously at 0 °C while 30% hydrogen peroxide (40 ml) was added dropwise over 1 h. The organic phase was separated, washed with aqueous sodium hydrogencarbonate and water, dried ($MgSO_4$), and chromatographed on silica (100 g). Elution with ether afforded di-t-butylphosphinic chloride (1.8 g, 9.2 mmol, 50%), m.p. 78—81 °C (lit.,[8] 80.1—80.9 °C) (from light petroleum), δ($CDCl_3$) 1.35 (d, J_{PH} 16 Hz). This phosphinic chloride was also prepared by passing dry oxygen through a solution of the chlorophosphine in xylene at 100 °C.

Di-isopropylphosphinic Chloride.—Di-isopropylphosphinic acid was prepared and converted into the phosphinic chloride as previously described.[5]

Diethylphosphinic Chloride.—(i) Tetraethylbiphosphine disulphide[9] (*ca.* 0.15 mol) in water (300 ml) was oxidised[10] by dropwise addition of 30% hydrogen peroxide (50 ml) at 80 °C. After boiling under reflux for 1 h, the precipitated sulphur was removed by filtration and a slight excess of freshly precipitated silver oxide added. The suspension was heated for 5 min, filtered, and the volume reduced (rotary evaporator) to 50 ml. The mixture was stirred vigorously with 12M hydrochloric acid (50 ml) and the precipitate filtered off. Removal of water (rotary evaporator) from the filtrate followed by distillation gave diethylphosphinic acid (16.0 g, 43%), b.p. 174 °C at 1.5 mmHg (lit.,[11] 194—195 °C at 21 mmHg), δ($CDCl_3$) 12.2 (1 H, s), 1.67 (4 H, dq, J_{PH} 14, J_{HH} 7 Hz), and 1.13 (6 H, dt, J_{PH} 18, J_{HH} 7 Hz).

(ii) The acid was treated with thionyl chloride (as previously described for the isopropyl analogue[5]) to give diethylphosphinic chloride (94%), b.p. 54—56 °C at *ca.* 0.5 mmHg (lit.,[12] 54 °C at 0.25 mmHg), δ($CDCl_3$) 2.3—1.9 (4 H, m) and 1.30 (6 H, dt, J_{PH} 20.5, J_{HH} 7 Hz).

Di-t-butylphosphinic Azide.—Di-t-butylphosphinic chloride (1.7 g, 8.6 mmol) was stirred vigorously with sodium azide (1.3 g, 20 mmol) and pyridine (1.7 g, 21.5 mmol) in dry dimethylformamide (15 ml) for 4 h at 95—105 °C (bath temp.). Ether (30 ml) was added, the mixture was filtered, and volatile matter was removed. Distillation afforded *di-t-butylphosphinic azide* (1.4 g, 80%), b.p. 75—80 °C (oven temp.) at 0.5 mmHg, $\nu_{max.}$ (liquid film) 2 145 (N_3) and 1 280 cm^{-1} (P=O), δ($CDCl_3$) 1.28 (d, J_{PH} 15 Hz) (Found: C, 45.8; H, 8.8; N, 20.0. $C_8H_{18}N_3OP \cdot 0.35H_2O$ requires C, 45.9; H, 9.0; N, 20.05%); the azide could not be obtained completely free of water.

Di-isopropylphosphinic Azide.—Di-isopropylphosphinic chloride (2.4 g, 14.2 mmol) in dimethylformamide (7 ml) was added dropwise to a vigorously stirred mixture of sodium azide (1.85 g, 28 mmol) and pyridine (2.55 g, 32 mmol) in dimethylformamide (10 ml) at room temperature. After a further 1 h the reaction was worked up as above to give *di-isopropylphosphinic azide* (1.8 g, 10.3 mmol, 74%), b.p. 72—78 °C (oven temp.) at 0.5 mmHg, $\nu_{max.}$ (liquid film) 2 150 (N_3) and 1 270 and 1 210 cm^{-1} (P=O), δ($CDCl_3$) 2.06 (2 H, double septet, $J_{HH} \sim J_{PH} \sim 7$ Hz), 1.22 (6 H, dd, J_{PH} 17, J_{HH} 7 Hz), and 1.18 (6 H, dd, J_{PH} 17, J_{HH} 7 Hz) (Found: C, 40.4; H, 8.0; N, 23.8. $C_6H_{14}N_3OP \cdot 0.15H_2O$ requires C, 40.5; H, 8.1; N, 23.6%); the product could not be obtained entirely free of water.

Diethylphosphinic Azide.—Diethylphosphinic chloride (2.8 g, 19.9 mmol) in dry acetonitrile (30 ml) was added dropwise to a vigorously stirred, ice-cooled, mixture of sodium azide (2.6 g, 40 mmol) and pyridine (3.75 g, 47 mmol) in acetonitrile (20 ml). After 4 h at room temperature the mixture was filtered and distilled to give diethylphosphinic azide (1.8 g, 61%), b.p. 95 °C (oven temp.) at 7 mmHg (lit.,[13] 97 °C at 8 mmHg), $\nu_{max.}$ (liquid film) 2 150 (N_3) and 1 270 and 1 205 cm^{-1} (P=O), δ($CDCl_3$) 1.84 (4 H, dq, J_{PH} 12, J_{HH} 7 Hz) and 1.21 (6 H, dt, J_{PH} 18, J_{HH} 7 Hz).

Methyl Diethylphosphinate.—Addition of diethylphosphinic chloride to a solution of sodium methoxide in methanol gave methyl diethylphosphinate (29%), b.p. 86—92 °C (oven temp.) at 13 mmHg (lit.,[14] 86 °C at 12 mmHg), $\nu_{max.}$ (liquid film) 1 200, 1 050, 1 025, 795, and 775 cm^{-1}, δ($CDCl_3$) 3.68 (3 H, d, J_{PH} 10 Hz), 1.71 (4 H, dq, J_{PH} 14, J_{HH} 7 Hz), and 1.13 (6 H, dt, J_{PH} 17, J_{HH} 7 Hz).

Methyl P-*Isopropylphosphonamidate* (10).—A solution of methanol (0.126 g, 4.0 mmol) and pyridine (0.315 g, 4.0 mmol) in ether (5 ml) was added dropwise (0.5 h) with stirring to isopropylphosphonic dichloride[15] (0.641 g, 3.98 mmol) in ether. After a further 1 h the mixture was filtered and dripped into a solution of ammonia (large excess) in ether (10 ml). After 2 h volatile material was evaporated off and the residue extracted with hot chloroform (2 × 30 ml) to give *methyl* P-*isopropylphosphonamidate* (0.038 g, 7%), m.p. 84—86 °C (from light petroleum–tetrachloromethane), $\nu_{max.}$ (Nujol) 3 310, 3 240, 3 130, and 1 575 (NH_2) and 1 195 cm^{-1} (P=O), δ($CDCl_3$) 3.58 (3 H, d, J_{PH} 10 Hz), *ca.* 2.8br (2 H, NH_2), *ca.* 1.9 (1 H, m), and 1.17 (6 H, dd, J_{PH} 18, J_{HH} 6 Hz), *m/e* 137 (6%) (M^+), 95 (100) ($M^+ - C_3H_6$), and 94 (30) ($M^+ - C_3H_7$) (Found: C, 34.9; H, 8.75; N, 10.2. $C_4H_{12}NO_2P$ requires C, 35.0; H, 8.8; N, 10.2%).

Di-isopropylphosphinic N-*Methoxyamide.*—Sodium wire (0.34 g, 15 mg atom) was added in small pieces to *O*-methylhydroxylamine hydrochloride (1.23 g, 15 mmol) in ethanol (10 ml). After 0.5 h the mixture was filtered and the filtrate cooled (ice) and stirred while di-isopropylphosphinic chloride (1.0 g, 5.9 mmol) was slowly added. Stirring was continued for 48 h at room temperature. A portion of the reaction mixture (equivalent to 1.6 mmol of phosphinic chloride) was chromatographed on a layer of alumina. Development with 6% methanol in ether gave the *methoxyamide* (0.133 g, 47%), m.p. 57—58.5 °C (sealed tube) [from light petroleum (b.p. 40—60 °C) at low temperature], *m/e* 179 (20%) (M^+), 149 (13) ($M^+ - CH_2O$), 133 (51) ($M^+ - NHOMe$), 107 (100) ($M^+ - CH_2O - C_3H_6$), 106 (60), and 105 (40), $\nu_{max.}$ (Nujol) 3 100 (NH) and 1 180 and 1 160 cm^{-1} (P=O), δ($CDCl_3$) 6.2br (1 H, s, NH), 3.55 (3 H, s), 2.4—1.6 (2 H, m), 1.23 (6 H, dd, J_{PH} 16, J_{HH} 7 Hz), and 1.21 (6 H, dd, J_{PH} 16, J_{HH} 7 Hz) (Found: C, 46.3; H, 10.1; N, 7.55. $C_7H_{18}NO_2P$ requires C, 46.9; H, 10.1; N, 7.8%).

Photochemical Reactions.—These reactions employed a 125-W medium-pressure mercury lamp in a water-cooled quartz envelope immersed in the stirred reaction mixture. Reaction was monitored by means of a gas burette connected to the reaction vessel and irradiation was continued

until gas evolution ceased. The volume of gas collected was generally very close to that expected assuming one mole of azide produces one mole of nitrogen. Solvent was evaporated from the reaction mixture and the residue (or a measured fraction of it) was worked-up as detailed below. Yields refer to material after chromatographic separation but before final purification. Each photochemical investigation included a control reaction in which a solution of the azide in the appropriate solvent was kept in the dark at room temperature. After a time equal to that employed in the photolysis, the solvent was evaporated off and the residue examined by i.r. and n.m.r. spectroscopy. In all except two cases the azide was recovered completely unchanged. Diethylphosphinic azide in methanol was almost completely solvolysed to methyl diethylphosphinate. Di-isopropylphosphinic azide in t-butylamine was partially converted into a product (not *N'P*-di-isopropyl-*N*-t-butylphosphonic diamide by g.l.c. examination) thought to be di-isopropylphosphinic anhydride, m.p. 90—91 °C (from light petroleum), *m/e* 282 (30%) (M^+), 240 (30), 239 (40), and 197 (100), $\nu_{max.}$ (Nujol) 1 215 (P=O) and 960 cm^{-1} (P–O–P).

Di-t-butylphosphinic Azide.—(i) *In methanol.* The azide (0.541 g, 2.67 mmol) in methanol (60 ml) was irradiated for 19 h and the mixture was then chromatographed on a layer of alumina. Development with ether afforded *methyl* NP-*di-t-butylphosphonamidate* (6; R = Bu^t, X = OMe) (0.390 g, 71%), m.p. 98—99 °C (from light petroleum), *m/e* 192 (100%) ($M^+ - CH_3$), $\nu_{max.}$ (Nujol) 3 220 (NH) and 1 190 cm^{-1} (P=O), δ($CDCl_3$) 3.50 (3 H, d, J_{PH} 11 Hz), *ca.* 2.0br (1 H), 1.30 (9 H, s), and 1.10 (9 H, d, J_{PH} 15 Hz) (Found: C, 52.3; H, 10.8; N, 6.5. $C_9H_{22}NO_2P$ requires C, 52.2; H, 10.7; N, 6.75%). Development with 3% methanol in ether gave *di-t-butylphosphinic* N-*methoxyamide* (9; R = Bu^t, X = OMe) (0.045 g, 8%), m.p. 170.5—171.5 °C (from light petroleum), *m/e* 207 (22%) (M^+), 177 (15) ($M^+ - CH_2O$), and 121 (100) ($M^+ - CH_2O - C_4H_8$), $\nu_{max.}$ (Nujol) 3 100 (NH) and 1 160 cm^{-1} (P=O), δ($CDCl_3$) 6.0br (1 H), 3.52 (3 H, s), and 1.27 (18 H, d, J_{PH} 13 Hz) (Found: C, 52.4; H, 10.8; N, 6.5. $C_9H_{22}NO_2P$ requires C, 52.2; H, 10.7; N, 6.75%).

(ii) *In ethanol.* The azide (0.542 g, 2.67 mmol) in ethanol (100 ml) was irradiated for 20.5 h, and a portion of the reaction mixture (equivalent to 1.07 mmol of azide) was chromatographed on a layer of alumina. Development with 6% methanol in ether gave *ethyl* NP-*di-t-butylphosphonamidate* (6; R = Bu^t, X = OEt) (0.147 g, 62%), m.p. 120—122 °C (sealed tube) [from light petroleum (b.p. 40—60 °C)], *m/e* 206 (100%) ($M^+ - CH_3$) and 178 (12) ($M^+ - CH_3 - C_2H_4$), $\nu_{max.}$ (Nujol) 3 230 (NH) and 1 190 cm^{-1} (P=O), δ($CDCl_3$) 3.98 (2 H, dq, $J_{PH} = J_{HH} = 7$ Hz), 2.7br (1 H), 1.32 (9 H, s), 1.25 (largely hidden but consistent with 3 H, t, J_{HH} 7 Hz), and 1.12 (9 H, d, J_{PH} 16 Hz) (Found: C, 54.4; H, 10.9; N, 6.0. $C_{10}H_{24}NO_2P$ requires C, 54.3; H, 10.9; N, 6.3%). A product having a smaller R_F was isolated and identified as di-t-butylphosphinic amide (0.045 g, 24%), m.p. 199—200 °C (from benzene) (lit.,[5] 199—200 °C), by spectroscopic comparison with an authentic sample.[5]

(iii) *In isopropyl alcohol.* The azide (0.554 g, 2.73 mmol) in isopropyl alcohol (100 ml) was irradiated for 5 h. Chromatography of a portion of the reaction mixture (equivalent to 1.09 mmol of azide) as in (ii) afforded *isopropyl* NP-*di-t-butylphosphonamidate* (6; R = Bu^t, X = OPr^i) (0.069 g, 27%), m.p. 148.5—150 °C [from light petroleum (b.p. 40—60 °C)], *m/e* 220 (50%) ($M^+ - CH_3$), 208 (40) ($M^+ - C_2H_3$), and 178 (100) ($M^+ - CH_3 - C_3H_6$), $\nu_{max.}$ (Nujol) 3 250 (NH) and 1 190 cm^{-1} (P=O), δ($CDCl_3$) 4.9—4.4 (1 H, m), 1.95br (1 H), 1.34 (9 H, s), 1.28 (3 H, d, J_{HH} 6 Hz), 1.25 (3 H, d, J_{HH} 6 Hz), and 1.12 (9 H, d, J_{PH} 16 Hz) (Found: C, 56.0; H, 11.0; N, 5.9. $C_{11}H_{26}NO_2P$ requires C, 56.1; H, 11.1; N, 5.95%). The major product, di-t-butylphosphinic amide (0.123 g, 64%), was isolated and characterised as in (ii).

(iv) *In t-butyl alcohol.* The azide (0.554 g, 2.73 mmol) in t-butyl alcohol (100 ml) was irradiated for 5 h, and a portion of the reaction mixture (equivalent to 1.09 mmol of azide) was chromatographed on a layer of alumina. Development with ether yielded *t-butyl* NP-*di-t-butylphosphonamidate* (6; R = Bu^t, X = OBu^t) (0.170 g, 63%), m.p. 137—139 °C (sealed tube) [from light petroleum (b.p. 40—60 °C)], *m/e* 234 (24%) ($M^+ - CH_3$) and 178 (100) ($M^+ - CH_3 - C_4H_8$), $\nu_{max.}$ (Nujol) 3 280 (NH), 1 240, 1 190 (P=O), and 990 cm^{-1}, δ($CDCl_3$) 2.6br (1 H), 1.43 (9 H, s), 1.30 (9 H, s), and 1.07 (9 H, d, J_{PH} 16 Hz) (Found: C, 57.4; H, 11.2; N, 5.6. $C_{12}H_{28}NO_2P$ requires C, 57.8; H, 11.3; N, 5.6%). Development with 6% methanol in ether afforded di-t-butylphosphinic amide (0.013 g, 6.5%), characterised as in (ii), and a small amount of a compound having a larger R_F; this was not obtained pure but was tentatively identified as di-t-butylphosphinic *N*-t-butoxyamide (9; R = Bu^t, X = OBu^t), *m/e* 193 (40%) ($M^+ - C_4H_8$), 177 (35) ($M^+ - C_4H_8O$), and 121 (100) ($M^+ - C_4H_8O - C_4H_8$), $\nu_{max.}$ (Nujol) 3 070 (NH) and 1 100 cm^{-1} (P=O), δ($CDCl_3$) 5.4br (1 H), 1.30 (18 H, d, J_{PH} 14 Hz), and 1.22 (9 H, s).

(v) *In t-butylamine.* The azide (0.500 g, 2.46 mmol) in t-butylamine (100 ml) was irradiated for 27 h. Chromatography on a column of alumina and elution with ether and then methanol in ether gave *NN'P*-tri-t-butylphosphonic diamide (6; R = Bu^t, X = $NHBu^t$) (0.451 g, 74%), m.p. 178—180 °C (sealed tube) (from light petroleum) (lit.,[16] 181—182 °C), *m/e* 248 (5%) (M^+), 233 (100) ($M^+ - CH_3$), and 191 (100) ($M^+ - C_4H_9$), $\nu_{max.}$ (Nujol) 3 280 (NH) and 1 170 cm^{-1} (P=O), δ($CDCl_3$) *ca.* 1.9br (2 H), 1.28 (18 H, s), and 1.08 (9 H, d, J_{PH} 14 Hz).

Di-isopropylphosphinic Azide.—(i) *In methanol.* The azide (0.794 g, 4.52 mmol) in methanol (100 ml) was irradiated for 17 h. Chromatography of a portion of the reaction mixture (equivalent to 2.71 mmol of azide) on a layer of alumina and development with 6% methanol in ether afforded *methyl* NP-*di-isopropylphosphonamidate* (6; R = Pr^i, X = OMe) (0.345 g, 71%) which was obtained as a waxy solid by sublimation (80 °C at 2 mmHg), *m/e* 164 (100%) ($M^+ - CH_3$), $\nu_{max.}$ (Nujol) 3 180 (NH) and 1 195, 1 160, and 1 140 cm^{-1} (P=O), δ($CDCl_3$) 3.65 (3 H, d, J_{PH} 10.5 Hz), *ca.* 3.5 (1 H, m, $NCHMe_2$), 2.5—1.5 (2 H, m, NH and $PCHMe_2$), 1.18 (6 H, d, J_{HH} 6 Hz), and 1.17 (6 H, dd, J_{PH} 17, J_{HH} 7 Hz) (Found: C, 46.8; H, 10.3; N, 7.7. $C_7H_{18}NO_2P$ requires C, 46.9; H, 10.1; N, 7.8%). Two minor products having smaller R_F values were isolated as a mixture. One component, purified by crystallisation of the mixture from benzene–light petroleum, was shown to be di-isopropylphosphinic amide (0.020 g, 5%), m.p. 135—137 °C (lit.,[5] 135—137.5 °C), by spectroscopic comparison with an authentic sample.[5] The other component was not obtained pure but had an n.m.r. spectrum consistent with it being di-isopropylphosphinic *N*-methoxyamide. On repetition of the experiment a pure sample of di-isopropylphosphinic *N*-methoxyamide (9; R = Bu^t, X = OMe) was obtained, m.p. 57—59 °C (from light petroleum),

i.r. and n.m.r. spectra as for the authentic material. Examination of the original reaction mixture by g.l.c. (3% OV 17 at 128 °C) established the absence (<1%) of methyl *P*-isopropylphosphonamidate [authentic sample, t_R 7.0 min; methyl *NP*-di-isopropylphosphonamidate, t_R 7.8 min].

(ii) *In ethanol.* The azide (0.515 g, 2.94 mmol) in ethanol (100 ml) was irradiated for 20 h. A portion of the reaction mixture (equivalent to 1.47 mmol of azide) was chromatographed on a layer of alumina. Development with 3% methanol in ether afforded *ethyl* NP-*di-isopropylphosphonamidate* (6; R = Pr^i, X = OEt) (0.107 g, 38%) as a waxy solid after sublimation at 90 °C and 2 mmHg; *m/e* 193 (3%) (M^+) and 178 (100) ($M^+ - CH_3$), $\nu_{max.}$ (Nujol) 3 190 (NH) and 1 200, 1 165, 1 145 cm^{-1} (P=O), δ($CDCl_3$) 4.03 (2 H, m, OC*H*$_2$Me), 3.43 (1 H, m, NC*H*Me$_2$), *ca.* 2.35br (1 H, t, N*H*), 2.2—1.5 (1 H, m, PC*H*Me$_2$), and 1.4—1.0 [15 H; tentative analysis: 1.30 (3 H, t, J_{HH} 7 Hz), 1.16 (3 H, dd, J_{PH} 17.5, J_{HH} 7 Hz), 1.17 (3 H, dd, J_{PH} 17.5, J_{HH} 7 Hz), and 1.18 (6 H, d, J_{HH} 7 Hz)]; deuterium exchange removed δ 2.35 and simplified δ 3.43 (Found: C, 49.8; H, 10.4; N, 7.2. $C_8H_{20}NO_2P$ requires C, 49.7; H, 10.4; N, 7.25%). A product having a smaller R_F was isolated and identified as di-isopropylphosphinic amide (0.100 g, 46%) as in (i).

(iii) *In isopropyl alcohol.* The azide (0.504 g, 2.88 mmol) in isopropyl alcohol (100 ml) was irradiated for 3 h. Chromatography as in (ii) gave di-isopropylphosphinic amide (0.374 g, 87%), m.p. 134—136 °C, spectra as for the authentic amide. A trace of a product (possibly isopropyl *NP*-di-isopropylphosphonamidate) having a larger R_F was evident, but this compound was not isolated.

(iv) *In t-butylamine.* The azide (0.532 g, 3.04 mmol) in t-butylamine (100 ml) was irradiated for 21 h. A portion of the reaction mixture (equivalent to 1.52 mmol of azide), chromatographed as in (ii) above, afforded N'P-*di-isopropyl*-N-*t-butylphosphonic diamide* (6; R = Pr^i, X = NHBu^t) (0.246 g, 74%), m.p. 163—164 °C (sealed tube) [from light petroleum (b.p. 40—60 °C)], *m/e* 220 (3%) (M^+), 205 (100) ($M^+ - CH_3$), and 177 (16) ($M^+ - C_3H_7$), $\nu_{max.}$ (Nujol) 3 220 (NH) and 1 180 cm^{-1} (P=O), δ($CDCl_3$) 3.49 (1 H, m, NC*H*Me$_2$), *ca.* 2.0br (2 H, NH), 2.0—1.5 (1 H, m, PC*H*Me$_2$), 1.35 (9 H, s), 1.17 (6 H, d, J_{HH} 6 Hz), and 1.14 (6 H, dd, J_{PH} 17, J_{HH} 6 Hz); exchange with deuterium eliminates δ 2.0 and simplifies δ 3.49 (Found: C, 54.7; H, 11.6; N, 12.8. $C_{10}H_{25}N_2OP$ requires C, 54.5; H, 11.4; N, 12.7%).

Diethylphosphinic Azide.—In methanol. The azide (0.430 g, 2.92 mmol) in methanol (60 ml) was irradiated for 23 h. The n.m.r. spectrum of the crude product indicated two principal components in a ratio of *ca.* 2 : 1. Chromatography on a column of alumina and elution with ether containing methanol (0—3%) afforded the major component, methyl diethylphosphinate (0.189 g, 48%), b.p. 80 °C (oven temp.) at 8 mmHg, i.r. and n.m.r. spectra as for the authentic ester, followed by *methyl* NP-*diethylphosphonamidate* (6; R = Et, X = OMe) (0.077 g, 17%), b.p. 110 °C (oven temp.) at 8 mmHg, *m/e* 151 (20%) (M^+), 136 (100) ($M^+ - CH_3$), 122 (80), and 107 (80), $\nu_{max.}$ (liquid film) 3 210 (NH) and 1 200 cm^{-1} (P=O), δ($CDCl_3$) 3.62 (3 H, d, J_{PH} 11 Hz), 2.93 (2 H, ddq, $J_{HH} = J_{HH} = J_{PH} = 7$ Hz, NC*H*$_2$Me), 2.54br (1 H, NH), 1.95—1.45 (2 H, m, PC*H*$_2$Me), 1.13 (3 H, t, J_{HH} 7 Hz), and 1.12 (3 H, dt, J_{PH} 19.5, J_{HH} 7 Hz); exchange with D_2O eliminates δ 2.54 and simplifies δ 2.93 to dq (Found: C, 38.3; H, 9.3; N, 8.9. $C_5H_{14}NO_2P \cdot 0.3H_2O$ requires C, 38.4; H, 9.4; N, 8.95%). It is believed that there were substantial lossess of products during work-up and isolation as a result of their volatility and (for the phosphonamidate) ease of hydrolysis.

When photolysis was carried out at *ca.* −70 °C (external cooling with solid CO_2–acetone) to inhibit non-photochemical reactions, the yield of phosphinate was reduced and that of phosphonamidate increased [ratio 1 : 2 (n.m.r.)].

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