Photolysis of 1-Azidophosphetan Oxides: Ring Expansion to 2-Methoxy-1,2-azaphospholidine 2-Oxides and Ring Opening to Methyl Alk–yl-phosphonamidates in Methanol [1]

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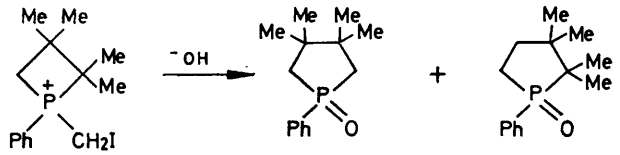
Irradiation of 1-azido-2,2,4,4-tetramethylphosphetan 1-oxide (4) in methanol leads by ring expansion to 2-methoxy-3,3,5,5-tetramethyl-1,2-azaphospholidine 2-oxide (17), and by ring opening to methyl (1,1,3-trimethylbut-3-enyl)phosphonamidate (20). The 2,2,3,3-tetramethyl analogue (5) behaved similarly, except that two isomeric ring expansion products (21) and (23) were obtained, in relative yields indicative of the absence of any marked preference for migration of the primary or tertiary ring-carbon atom. In the case of 1-azido-2,2,3,4,4-pentamethylphosphetan 1-oxide [(6), single geometrical isomer], the product (25) of ring expansion was formed as a mixture of geometrical isomers having the methoxy-group *cis* or *trans* to the 4-methyl group. The possible involvement of nitrene and metaphosphonimidate intermediates in these reactions is briefly discussed.

PHOSPHETANS and their derivatives have a marked tendency to react with expansion or opening of the four-membered ring. Thus, for example, the iodomethylphosphetanium salt (1) gives the isomeric phospholan oxides (2) and (3) on alkaline hydrolysis.[2] Here, as in the other cases of ring expansion so far reported,[2-4] a



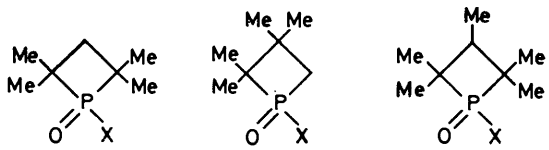
carbon atom in the ring migrates from phosphorus to an exocyclic carbon centre. In the hope of observing ring expansion with migration from phosphorus to nitrogen, we have prepared the azido-phosphetan oxides (4)—(6) and examined their photolysis in methanol.

The decomposition reactions of phosphinic azides, $R_2P(O)N_3$, have hitherto received little attention. Reichle [5] found evidence for migration of a phenyl group from phosphorus to nitrogen in the vacuum pyrolysis of $Ph_2P(O)N_3$, but he did not investigate the products in detail. From the copper-catalysed pyrolysis of the related azide $Ph_2P(NTs)N_3$, Bock and Wiegräbe [6] obtained products derived (formally) from the unrearranged nitrene. Photolysis of phosphinic azides has not previously been studied, although phosphorodiamidic azides, $(RNH)_2P(O)N_3$ are reported to be unaffected by irradiation with u.v. light.[7]

[1] Preliminary account of part of this work, M. J. P. Harger, *Chem. Comm.*, 1971, 442.
[2] J. R. Corfield, M. J. P. Harger, J. R. Shutt, and S. Trippett, *J. Chem. Soc.* (*C*), 1970, 1855.
[3] W. Hawes and S. Trippett, *J. Chem. Soc.* (*C*), 1969, 1465.
[4] S. E. Fishwick, J. Flint, W. Hawes, and S. Trippett, *Chem. Comm.*, 1967, 1113; S. E. Cremer and R. J. Chorvat, *Tetrahedron Letters*, 1968, 413; S. E. Cremer, *Chem. Comm.*, 1968, 1132.

RESULTS AND DISCUSSION

The required phosphinic azides (4)—(6) were obtained by reaction of the appropriate chlorophosphetan oxides (7)—(9) with sodium azide. Conversion of chloride (9) into the azide (6) was largely complete after 24 h in pyridine at 110°. Subsequently it was found that the azides (4) and (5) were formed readily in dimethylformamide at room temperature, and similar conditions would doubtless prove more convenient for the preparation of (6) as well. All the azides were distilled under reduced pressure without apparent decomposition.



X = N_3	(4)	(5)	(6)
X = Cl	(7)	(8)	(9)
X = OMe	(10)	(11)	(12)
X = NH_2	(13)	(14)	(15)

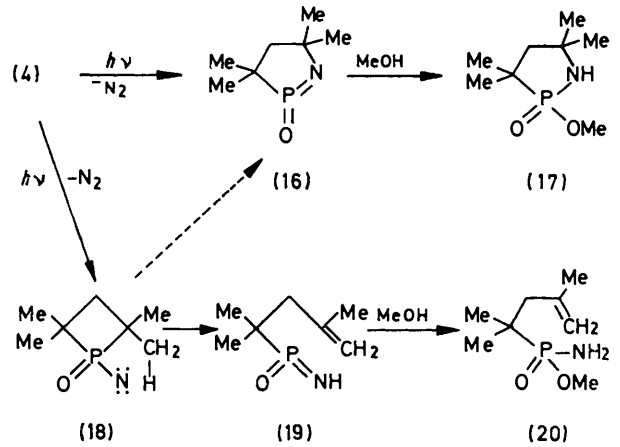
In the absence of light, the only reaction of the azides (4)—(6) in methanol was slow formation of the corresponding methyl esters (10)—(12), and even with (5), the least hindered and most reactive azide, this nucleophilic attack by the solvent did not seriously interfere with the photochemical reaction. Irradiation of methanolic solutions of the azides (4)—(6) at room temperature with a mercury

[5] W. T. Reichle, *Inorg. Chem.*, 1964, **3**, 402.
[6] H. Bock and W. Wiegräbe, *Angew. Chem. Internat. Edn.*, 1962, **1**, 265; *Chem. Ber.*, 1966, **99**, 1068.
[7] R. J. W. Cremlyn, B. B. Dewhurst, and D. H. Wakeford, *J. Chem. Soc.* (*C*), 1971, 3011; H. J. Vetter, *Z. Naturforsch.*, 1964, **19b**, 167 (*Chem. Abs.*, 1964, **60**, 13,129*g*).

lamp caused decomposition, with concomitant evolution of nitrogen, to proceed steadily to completion.

The product from the photolysis of azide (4) was an oily solid, seen by g.l.c. to contain two principal components in the approximate ratio 3 : 1. The individual products were isolated by crystallisation and chromatography. From their mass spectra (M^+ 191) and elemental analyses, it was clear that they were isomers ($C_8H_{18}NO_2P$) derived formally from the azide by elimination of N_2 and addition of methanol.

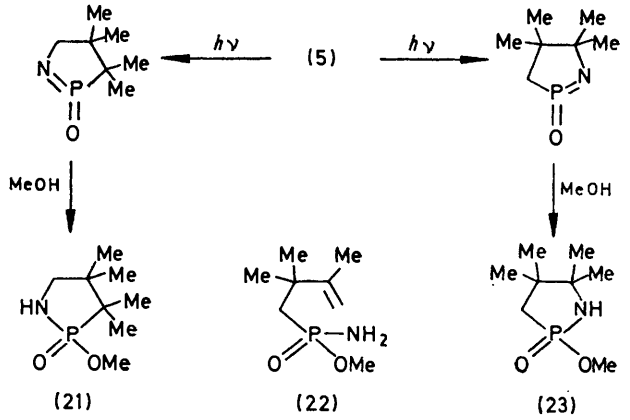
The major product, the cyclic phosphonamidic ester (17) (62%) was characterised by its n.m.r. spectrum, the NH·P(O)OMe system giving rise to doublets at δ 5·18br (1H, J_{PH} 10 Hz, exchanged with D_2O) and 3·57 (3H, J_{PH} 10 Hz), while the pairs of Me groups on C-3 and C-5 appear at δ 1·24—1·13 as two doublets (J_{PH} 15 Hz) and two singlets respectively. I.r. absorptions attributable to NH (3180 cm^{-1}) and MeO·P:O (1240, 1215, 1180, 1030, and 1015 cm^{-1}) groups are in accord with the structure (17). By analogy with the formation of isocyanates in the Curtius rearrangement of acyl azides,[8] it seems reasonable to suppose that the phosphonamidic ester (17) is formed by way of an intermediate metaphosphonimidate (16) (Scheme 1). This species might itself result from rearrangement of a phosphinyl nitrene (18), although it is equally likely that ring expansion, with migration from phosphorus to nitrogen, occurs at the same time as the expulsion of N_2 from an excited state of the azide.



SCHEME 1

The minor product (16%) from the photolysis also contains the MeO·P:O grouping, but in other respects it differs strikingly from (17). In particular, the presence of NH_2 [$\nu_{max.}$ 3325, 3240, and 3130 cm^{-1}; δ 4·03br (d, J_{PH} 6 Hz, exchanged with D_2O)] and C=CH_2 ($\nu_{max.}$ 1640 cm^{-1}; δ 4·77 and 4·58) groups suggests the acyclic phosphonamidic ester structure (20). As would be expected, the allylic CH_2 and Me protons are deshielded (δ 2·24 and 1·77). The slight broadening of the 6H doublet (J_{PH} 16 Hz) at δ 1·08 may reflect the non-equivalence of the two Me groups on the carbon atom adjoining the chiral phosphorus. The mechanism of ring opening is unclear, although generation of the nitrene (18) (possibly in a triplet state) followed by intramolecular hydrogen transfer and formation of the acyclic metaphosphonimidate (19) (Scheme 1) is conceivable.

Unlike (4), the azide (5) lacks symmetry, and thus has two possible modes of ring expansion (Scheme 2). On photolysis in methanol an approximately equimolar mixture (40% total) of the isomeric cyclic phosphonamidates (21) and (23) was obtained. Chromatography and crystallisation afforded pure samples of the isomers, which could be readily differentiated from their n.m.r. spectra. Whereas the four Me groups in phosphonamidate (23) give rise to four singlet resonances, two of the Me groups in isomer (21) are coupled to the neighbouring phosphorus atom and appear in the spectrum as doublets (J_{PH} 16 Hz). The lack of any marked preference for migration of the primary or tertiary carbon atoms in the ring expansion of (5) is interesting, but we do not feel that it constitutes strong evidence for or against a nitrene intermediate.



SCHEME 2

A ring-opened product (13%) was also formed. Although it could not be isolated in a completely pure state, its n.m.r., i.r., and mass spectra allow structure (22) to be assigned with confidence. In contrast to the ring expansion reaction, ring opening seems to proceed entirely by cleavage of the tertiary C–P bond in (5). A ring-opening mechanism such as that considered above could not, of course, bring about cleavage of the primary C–P bond.

In azide (6), the identity of the two alkyl groups attached to phosphorus precludes a second mode of ring expansion. However, the presence of a single Me group on C-3 makes possible geometrical isomerism across the ring, not only in the azide but also in the anticipated ring-expansion product (25). Although the geometry of the azide (6) used in the present work is not known with certainty, its n.m.r. spectrum suggested that it was a single isomer. Moreover, since it was prepared from the *trans*-isomer [9] of chlorophosphetan oxide (9), and since

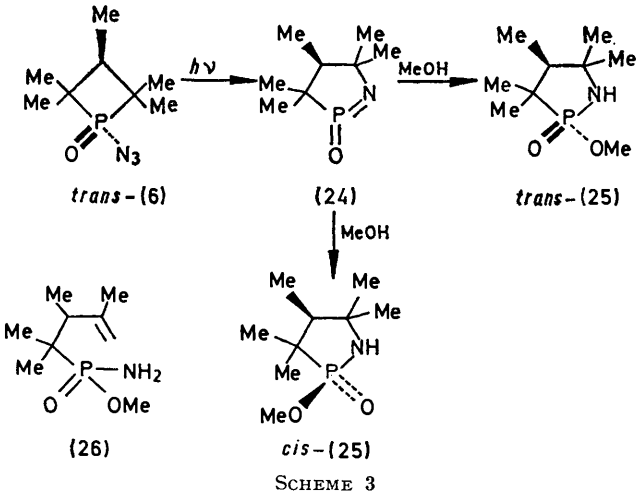
[8] P. A. S. Smith, in 'Molecular Rearrangements,' vol. 1, ed. P. de Mayo, Interscience, New York, 1963; J. H. Boyer, in 'Mechanisms of Molecular Migrations,' vol. 2, ed. B. Thyagarajan, Interscience, New York, 1969.

[9] J. J. McBride, E. Jungermann, J. V. Killheffer, and R. J. Clutter, *J. Org. Chem.*, 1962, **27**, 1833; Mazhar-ul-Haque, *J. Chem. Soc.* (*B*), 1970, 934.

(9) is known to react with a variety of nucleophiles with retention of configuration at phosphorus,[3,10] it seems probable that the azide group in (6) was in fact *trans* to the 3-methyl group. If the cyclic metaphosphonimidate (24) (Scheme 3) is indeed an intermediate in the photolysis of (6), attack of methanol from opposite sides could lead to isomeric cyclic methyl phosphonamidates (25) having the MeO group *trans* and *cis* to the 4-Me group. This possibility was realised, the ring-expanded product (25) (60%) being obtained as an unequal mixture of geometrical isomers (the MeO resonances of the two isomers, at δ 3·65 and 3·62, were in the approximate ratio 1 : 3). Repeated crystallisation of the isomeric mixture afforded a sample of the major isomer, but the minor isomer could not be obtained in a pure state.

Following our communication of this result, Westheimer and Wiseman [11] investigated the photolysis of both isomers of azide (6). They have found that whichever isomer is used, the same mixture of *cis*- and *trans*-phosphonamidate (25) is obtained. In addition, they have taken advantage of high pressure liquid chromatography to obtain pure samples of both isomers of phosphonamidate (25), and have isolated a number of interesting and mechanistically informative minor products.

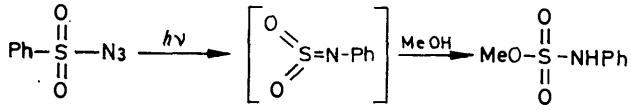
In common with the other azido-phosphetan oxides examined, azide (6) gave a ring-opened product (16%), in this case the methyl phosphonamidate (26). As noted



SCHEME 3

by Westheimer and Wiseman,[11] the presence of a second chiral centre in addition to phosphorus gives rise to diastereoisomerism in this compound. It may be that the wide melting range (107—115°) of the sample of (26) isolated in the present work is a consequence of its diastereoisomeric inhomogeneity.

In the foregoing discussion we have drawn an analogy between the ring-expansion reactions of azidophosphetan oxides and the Curtius rearrangement of acyl azides. In an acyl azide the carbonyl carbon atom is trigonal, and it might, therefore, be more appropriate to compare the behaviour of phosphinic azides (R_2PON_3), in which the phosphorus atom is tetrahedral, with that of sulphonyl azides (RSO_2N_3). The latter, in fact, generally give decomposition products derived from the sulphonyl nitrene ($RSO_2\ddot{N}$:) without any rearrangement.[12] However, Lwowski and his co-workers [13] did find methyl *N*-phenylsulphamate (28) among the products of photolysis of benzenesulphonyl azide (27) in methanol, and commented on the probable importance of hydrogen bonding by the solvent in the rearrangement of the azide. We likewise think it probable that the protic nature of the reaction medium is an important factor in the photochemical rearrangements of our phosphinic azides.



(27) (28)

Other products formed in the photolysis of benzenesulphonyl azide in methanol include the (formal) nitrene insertion product, $PhSO_2NHOMe$, and benzenesulphonamide.[13] In none of our phosphinic azide photolyses did we encounter analogous products, although only in the case of the phosphinamides (13)—(15) did we have authentic samples to assist in establishing their absence from the photolysis products.

EXPERIMENTAL

M.p.s were determined with a Kofler hot-stage apparatus. I.r. spectra were recorded with Perkin-Elmer 237 and 257 instruments, and n.m.r. spectra with a Varian T-60 spectrometer and tetramethylsilane as internal standard. Mass spectra were obtained using an A.E.I. MS9 instrument. G.l.c. analyses were performed on a Pye 104 flame ionisation chromatograph fitted with 1·5 m × 4 mm i.d. glass columns. Neutral alumina, Brockmann activity 1—2, was used for column chromatography. Petroleum refers to the fraction b.p. 60—80° unless otherwise indicated. Photochemical reactions employed a 125 W medium-pressure mercury lamp in a water-cooled quartz envelope, surrounded by the stirred reaction mixture. The solvent was anhydrous AnalaR methanol, and nitrogen evolution was followed by means of a gas burette connected to the reaction vessel.

2,4-*Dimethylpent*-2-*ene*.[14]—Iodine-catalysed dehydration of 2,4-dimethylpentan-2-ol and fractional distillation of the product using a spinning band column gave the alkene, b.p. 83·5—84° (lit.,[14] 81—83°), having purity >99% by g.l.c.

1-*Chloro*-2,2,4,4-*tetramethylphosphetan* 1-*Oxide* (7).[15]—A

[10] (*a*) S. E. Cremer and B. C. Trivedi, *J. Amer. Chem. Soc.*, 1969, **91**, 7200; (*b*) S. E. Cremer, *Chem. Comm.*, 1970, 616; (*c*) J. R. Corfield, R. K. Oram, D. J. H. Smith, and S. Trippett, *J.C.S. Perkin I*, 1972, 713; J. R. Corfield, N. J. De'ath, and S. Trippett, *Chem. Comm.*, 1970, 1502; Mazhar-ul-Haque, *J. Chem. Soc.* (*B*), 1970, 938.

[11] J. Wiseman and F. H. Westheimer, *J. Amer. Chem. Soc.*, 1974, **96**, 4262.

[12] D. S. Breslow, in ' Nitrenes,' ed. W. Lwowski, Interscience, New York, 1970; but see also R. A. Abramovitch and W. D. Holcomb, *Chem. Comm.*, 1969, 1298; J. Martin, O. Meth-Cohn, and H. Suschitzky, *ibid.*, 1971, 1319.

[13] W. Lwowski, R. DeMauriac, T. W. Mattingly, and E. Scheiffele, *Tetrahedron Letters*, 1964, 3285; W. Lwowski and E. Scheiffele, *J. Amer. Chem. Soc.*, 1965, **87**, 4359.

[14] G. Edgar, G. Calingaert, and R. E. Marker, *J. Amer. Chem. Soc.*, 1929, **51**, 1483.

[15] J. A. Miller, personal communication.

suspension of aluminium chloride (15·4 g, 0·115 mol) in dichloromethane (100 ml) containing phosphorus trichloride (15·8 g, 0·115 mol) was stirred and cooled in ice while a solution of 2,4-dimethylpent-2-ene (10·8 g, 0·110 mol) was added during 0·5 h. After stirring at room temperature for 20 h, the mixture was added over 0·5 h to vigorously stirred ice–water (800 ml). The layers were separated, the aqueous portion was extracted with dichloromethane (50 ml), and the combined organic portions were washed with water (50 ml) and dried ($CaCl_2$). Evaporation of the solvent left a pale brown oil (21·7 g) which was distilled. The fraction b.p. 83—91° at 3·5 mmHg (7·1 g) was crystallised from petroleum (b.p. 40—60°) at −50° to give 1-chloro-2,2,4,4-tetramethylphosphetan 1-oxide (5·3 g, 0·029 mol, 26%), m.p. *ca.* 20°, δ (CCl_4) 2·20—1·10 (2H, m, CH_2), 1·47 (6H, d, J_{PH} 20 Hz, MeC·P·CMe), and 1·38 (6H, d, J_{PH} 22 Hz, MeC·P·CMe), $\nu_{max.}$ (melt) 1260 and 1220 cm^{-1}. Redistillation of the crystallisation mother liquor together with higher and lower b.p. fractions from the original distillation afforded additional product (3·1 g) of *ca.* 90% purity (n.m.r.).

1-*Hydroxy*-2,2,3,3-*tetramethylphosphetan* 1-*Oxide*.—A suspension of aluminium chloride (53·2 g, 0·40 mol) in dichloromethane (500 ml) containing phosphorus trichloride (55·0 g, 0·40 mol) was stirred and cooled in ice while a solution of 2,3,3-trimethylbut-1-ene (39·2 g, 0·40 mol) in dichloromethane (100 ml) was added during 1 h. The mixture was stirred for 2 h at room temperature, and then cooled while iced water (250 ml) was added, the addition being very slow until exothermic reaction ceased. The aqueous layer was separated and extracted with dichloromethane (3 × 50 ml). The extracts were combined with the organic layer, the solvent evaporated, and the residue stirred with hot (steam-bath) 2M-NaOH solution (400 ml). After cooling, insoluble matter was removed by washing with ether (2 × 50 ml) and the aqueous solution was acidified with 12M-HCl (70 ml) and extracted with dichloromethane (2 × 100 ml, 3 × 50 ml). The extracts were dried (Na_2SO_4) and concentrated to a solid, which on crystallisation from petroleum (b.p. 40—60°) gave 1-hydroxy-2,2,3,3-tetramethylphosphetan 1-oxide (35·4 g, 0·205 mol, 51%), $\nu_{max.}$ (Nujol) *ca.* 2800—1800 (v br with shallow maxima at *ca.* 2600, 2250, and 2160, OH), 1670br (δ OH), and 1200 cm^{-1} (P:O), δ (CCl_4) 12·68 (1H, s, OH), 2·32 (2H, d, J_{PH} 16 Hz, CH_2), 1·13 (6H, d, J_{PH} 20 Hz, P·CMe_2), and 1·10 (6H, d, J_{PH} 1 Hz, Me_2C). An analytical sample had m.p. 168—170° (Found: C, 52·0; H, 9·2; P, 18·9. Calc. for $C_7H_{15}O_2P$: C, 51·8; H, 9·3; P, 19·1%). Gray and Cremer [16] have recently obtained material, m.p. 186—188°, by a similar method.

1-*Chloro*-2,2,3,3-*tetramethylphosphetan* 1-*Oxide* (8).—This was prepared immediately before use by heating a solution of the hydroxyphosphetan oxide (0·070 mol) and thionyl chloride (0·140 mol) in dry benzene (150 ml) under reflux in an atmosphere of nitrogen for 18 h. After evaporation of volatile material, benzene was added to the residue and then evaporated off to remove last traces of thionyl chloride. The product was pumped at 0·3 mmHg to give the chlorophosphetan oxide (8) as a pale yellow solid, $\nu_{max.}$ (Nujol) 1250 and 1220 cm^{-1}, δ (C_6H_6) 2·53—2·25 (2H, 4 lines, Δν 1, 15, and 1 Hz, CH_2), 1·09 (3H, d, J_{PH} 23 Hz, P·CMe), 0·92 (3H, d, J_{PH} 25 Hz, P·CMe), 0·77 (3H, d, J_{PH} 1 Hz, Me), and 0·72 (3H, s, Me). This material decomposed on standing, and no attempt was made to purify it further or obtain elemental analyses.

1-*Chloro*-2,2,c-3,4,4-*pentamethylphosphetan* r-1-*Oxide* (9).—This was prepared by the method of McBride *et al.*[9] and had m.p. 73—75° (lit.,[9] 72—75°).

1-*Azido*-2,2,4,4-*tetramethylphosphetan* 1-*Oxide* (4).—A solution of the chlorophosphetan oxide (7) (2·17 g, 12·0 mmol) in anhydrous dimethylformamide (15 ml) was stirred and cooled in ice while pyridine (0·95 g, 12·0 mmol) and sodium azide (1·56 g, 24·0 mmol) were added. After 4·5 h at room temperature, ether (20 ml) was added, insoluble matter was removed by filtration, and the filtrate was concentrated on a rotary evaporator. Distillation in a bulb-tube apparatus afforded 1-*azido*-2,2,4,4-*tetramethylphosphetan* 1-*oxide* (1·82 g, 9·7 mmol, 81%), b.p. 95—100° (oven temp.) at 2·5 mmHg, $\nu_{max.}$ (film) 2145 (N_3) and 1260 and 1210 cm^{-1} (P:O), δ (CCl_4) 2·03—1·05 (2H, m, CH_2), 1·41 (6H, d, J_{PH} 19 Hz, MeC·P·CMe), and 1·29 (6H, d, J_{PH} 19 Hz, MeC·P·CMe) (Found: C, 44·7; H, 7·9; N, 21·9. $C_7H_{14}N_3OP$ requires C, 44·9; H, 7·55; N, 22·45%).

1-*Azido*-2,2,3,3-*tetramethylphosphetan* 1-*Oxide* (5).—This was similarly prepared from the chlorophosphetan oxide (8) using a reaction time of 18 h. The *product* had b.p. 81° at 0·4 mmHg, $\nu_{max.}$ (film) 2140 (N_3) and 1250 and 1215 cm^{-1} (P:O), δ (C_6H_6) 2·25—1·92 (2H, 4 lines, Δν 5, 10, and 5 Hz, CH_2), 1·08 (3H, d, J_{PH} 21·5 Hz, P·CMe), 0·81 (3H, d, J_{PH} 22·5 Hz, P·CMe), 0·75 (3H, d, J_{PH} 1 Hz, Me), and 0·70 (3H, s, Me) (Found: C, 44·6; H, 7·9; N, 22·3. $C_7H_{14}N_3OP$ requires C, 44·9; H, 7·55; N, 22·45%).

1-*Azido*-2,2,3,4,4-*pentamethylphosphetan* 1-*Oxide* (6).—The chlorophosphetan oxide (9) (8·1 g, 0·042 mol) and sodium azide (3·9 g, 0·060 mol) were stirred in dry pyridine (30 ml) at 110° (bath temp.) under nitrogen for 24 h. Insoluble material was removed by filtration and the solvent evaporated. The residue was extracted with ether and the extract concentrated to give the crude azide (5·5 g, 0·027 mol, 65%). A trace of unchanged chlorophosphetan oxide was sublimed out by stirring the crude azide at 60° (bath temp.) and 0·2 mmHg. Distillation then gave 1-*azido*-2,2,3,4,4-*pentamethylphosphetan* 1-*oxide*, b.p. 80—82° at 0·2 mmHg, $\nu_{max.}$ (film) 2140 (N_3) and 1260 and 1210 cm^{-1} (P:O), δ (C_6H_6) 1·07 (6H, d, J_{PH} 20 Hz, MeC·P·CMe), 0·95 (6H, d, J_{PH} 20 Hz, MeC·P·CMe), and 0·50 (3H, dd, J_{HH} 7, J_{PH} 2 Hz, Me) (the CH resonance could not be distinguished) (Found: C, 47·4; H, 8·25; N, 20·5. $C_8H_{16}N_3OP$ requires C, 47·8; H, 8·0; N, 20·9%).

1-*Methoxy*-2,2,4,4-*tetramethylphosphetan* 1-*Oxide* (10).—The chlorophosphetan oxide (7) (0·18 g, 1·0 mmol) was added to sodium methoxide [from sodium (0·046 g)] in methanol (4 ml). After 3 h at room temperature, water (5 ml) and dichloromethane (8 ml) were added and the organic layer was separated, dried (Na_2SO_4), and distilled in a bulb–tube apparatus to give the methoxyphosphetan oxide * (0·16 g, 0·91 mmol, 91%), b.p. 115—120° (oven temp.) at 25 mmHg, $\nu_{max.}$ (film) 1255, 1215, and 1025 cm^{-1} (MeO·P:O), δ (CCl_4) 3·65 (3H, d, J_{PH} 10 Hz, OMe), 2·2—1·0 (2H, m, CH_2), 1·32 (6H, d, J_{PH} 18 Hz, MeC·P·CMe), and 1·21 (6H, d, J_{PH} 17 Hz, MeC·P·CMe).

The known compounds 1-methoxy-2,2,3,3-tetramethylphosphetan 1-oxide (11) [16] and 1-methoxy-2,2,3,4,4-pentamethylphosphetan 1-oxide (12) [3,10a] were similarly prepared.

1-*Amino*-2,2,3,3-*tetramethylphosphetan* 1-*Oxide* (14).—A solution of the chlorophosphetan oxide (8) (9·02 g, 0·05 mol) in ether (40 ml) was added dropwise to a stirred solution of ammonia (2·55 g, 0·15 mol) in ethanol (30 ml) at 0°. After a

* This compound was hygroscopic and could not be obtained completely free of water.

[16] G. A. Gray and S. E. Cremer, *J. Org. Chem.*, 1972, **37**, 3458.

further 3 h, ether (100 ml) was added, the mixture filtered, the filtrate concentrated, and the residue crystallised from petroleum (b.p. 40—60°)–benzene (2 : 1) to give the *amino-phosphetan oxide* (6·43 g, 0·04 mol, 80%), m.p. 130—133°, $\nu_{max.}$ (Nujol) 3240, 3200, and 3190 (NH_2), 1575 (δ NH_2), and 1185 and 1150 cm^{-1} (P:O), δ ($CDCl_3$) 3·30br (2H, s, NH_2), 2·50—2·23 (2H, m, 3 lines, Δν 1 and 15 Hz, CH_2), 1·23 (3H, d, J_{PH} 19 Hz, P·CMe), 1·18 (3H, d, J_{PH} 1 Hz, Me), 1·17 (3H, d, J_{PH} 20 Hz, P·CMe), and 1·12 (3H, d, J_{PH} 1 Hz, Me) (Found: C, 51·8; H, 9·9; N, 8·7. $C_7H_{16}NOP$ requires C, 52·2; H, 10·0; N, 8·7%).

1-*Amino*-2,2,4,4-*tetramethylphosphetan* 1-*Oxide* (13).—This *compound* was similarly prepared, and had m.p. 126·5—127·5°, $\nu_{max.}$ (Nujol) 3400, 3360, 3255, and 3120 (NH_2), 1545 (δ NH_2), and 1185 and 1150 cm^{-1} (P:O), δ ($CDCl_3$) 2·80br (2H, s, NH_2), 2·2—1·0 (2H, m, CH_2), 1·36 (6H, d, J_{PH} 17 Hz, MeC·P·CMe), and 1·23 (6H, d, J_{PH} 17·5 Hz, MeC·P·CMe) (Found: C, 52·2; H, 10·0; N, 8·7. $C_7H_{16}NOP$ requires C, 52·2; H, 10·0; N, 8·7%).

1-*Amino*-2,2,3,4,4-*pentamethylphosphetan* 1-*Oxide* (15).—This compound, m.p. 162—163°, $\nu_{max.}$ (Nujol) 3360, 3230, and 3120 (NH_2), 1555 (δ NH_2), and 1180 and 1155 cm^{-1} (P:O), δ ($CDCl_3$) 2·67br (2H, s, NH_2), 1·23 (6H, d, J_{PH} 18 Hz, MeC·P·CMe), 1·18 (6H, d, J_{PH} 19 Hz, MeC·P·CMe), and 0·89 (3H, dd, J_{HH} 7, J_{PH} 2 Hz, Me) (the CH resonance could not be distinguished), was previously [17] prepared in a similar manner.

Photolysis of 1-*Azido*-2,2,4,4-*tetramethylphosphetan* 1-*Oxide* (4) *in Methanol*.—A solution of the azide (1·678 g, 8·97 mmol) in methanol (60 ml) was irradiated for 27 h until N_2 evolution ceased. Examination of the reaction mixture by g.l.c. (3% Silicone OV-17, 175°) revealed the absence of starting azide (<1%) and the presence of two prominent products (R_t 3·35 and 4·8 min; ratio *ca.* 3 : 1).

The solvent was evaporated from a portion of the reaction mixture (corresponding to 7·72 mmol azide) and the oily solid residue was twice crystallised from petroleum to give the shorter R_t product, 2-*methoxy*-3,3,5,5-*tetramethyl*-1,2-*azaphospholidine* 2-*oxide* (17) (0·594 g), m.p. 126—128°, M^+ 191, $\nu_{max.}$ (Nujol) 3180 (NH), 1240, 1215, and 1180 (MeO·P:O), and 1030 and 1015 cm^{-1} (P·OMe), δ (CCl_4) 5·18br (1H, d, J_{PH} 10 Hz, exchanged with D_2O, NH), 3·57 (3H, d, J_{PH} 10 Hz, MeO), 1·93—1·47 (2H, m, CH_2), 1·24 (3H, d, J_{PH} 15 Hz, 3-Me), 1·24 (3H, s, 5-Me), 1·17 (3H, s, 5-Me), and 1·13 (3H, d, J_{PH} 15 Hz, 3-Me) (Found: C, 50·3; H, 9·5; N, 7·2. $C_8H_{18}NO_2P$ requires C, 50·25; H, 9·5; N, 7·3%).

The combined crystallisation mother liquors were chromatographed on alumina (55 g). Elution with ether gave an oil (0·043 g) containing two components (g.l.c.), the major one being identified as 1-methoxy-2,2,4,4-tetramethylphosphetan 1-oxide (10) (*ca.* 2%) by comparison of its R_t value and n.m.r. spectrum with those of an authentic specimen. Elution with ether containing increasing amounts (1—10%) of methanol gave additional (17) (0·323 g; total 4·81 mmol, 62%) followed by the longer R_t (4·8 min) product as a solid (0·234 g). Crystallisation from petroleum and sublimation at 70° and 0·1 mmHg afforded *methyl* (1,1,3-*trimethylbut*-3-*enyl*)*phosphonamidate* (20) (1·23 mol, 16% crude), m.p. 92—94°, M^+ 191, $\nu_{max.}$ (Nujol) 3325, 3240, and 3130 (NH_2), 1640 (C=C), 1560 (δ NH_2), 1205, 1190, and 1160 (MeO·P:O), and 1050 and 1035sh cm^{-1} (P·OMe), δ (CCl_4) 4·77 and 4·58 (each 1H, s with unresolved fine structure, C=CH_2), 4·03br (2H, d, J_{PH} 6 Hz, exchanged with D_2O, NH_2), 3·55 (3H, d, J_{PH} 10 Hz, MeO), 2·24br (2H, d, J_{PH} 9 Hz, CH_2·C=C), 1·77br (3H, s, Me·C=C), and 1·08br (6H, d, J_{PH} 16 Hz, Me_2C·P) (Found: C, 50·3; H, 9·5; N, 7·3. $C_8H_{18}NO_2P$ requires C, 50·25; H, 9·5; N, 7·3%).

Minor products having R_t 2·25 and 4·6 min were not isolated in a pure state or identified. 1-Amino-2,2,4,4-tetramethylphosphetan 1-oxide (13) was shown by g.l.c. (authentic specimen R_t 4·25 min) to be absent (<1%) from the products.

In a control experiment under the same conditions but without irradiation, the azide remained unchanged (i.r., n.m.r.) except for the appearance of a small g.l.c. peak (*ca.* 1%) having the same R_t as authentic methoxyphosphetan oxide (10).

Photolysis of 1-*Azido*-2,2,3,3-*tetramethylphosphetan* 1-*Oxide* (5) *in Methanol*.—The azide (1·95 g, 10·4 mmol) in methanol (50 ml) was irradiated for 22 h until N_2 evolution ceased. Evaporation of the solvent gave an oil, the bulk of which (corresponding to 9·85 mmol azide) was chromatographed on alumina (65 g). Elution with ether containing increasing amounts (1—12%) of ethanol gave an approximately equimolar mixture of two compounds [δ (CCl_4) includes 3·64 (d, J_{PH} 11 Hz) and 3·59 (d, J_{PH} 11 Hz)] (0·76 g). Earlier fractions containing an excess of one component (δ 3·59) were crystallised from petroleum (b.p. 40—60°) to give 2-*methoxy*-4,4,5,5-*tetramethyl*-1,2-*azaphospholidine* 2-*oxide* (23), m.p. 65—66°, M^+ 191, $\nu_{max.}$ (KBr) 3240 (NH), 1230, 1210, and 1170 (MeO·P:O), and 1040 cm^{-1} (P·OMe), δ (CCl_4) 4·92br (1H, d, J_{PH} *ca.* 6 Hz, NH), 3·59 (3H, d, J_{PH} 11 Hz, MeO), 1·66 (2H, d, J_{PH} 15 Hz, CH_2), 1·18 (3H, s, Me), 1·12 (6H, s, 2 × Me), and 1·08 (3H, s, Me), δ (C_6H_6) includes 1·13 (3H, s), 1·02 (3H, s), 0·97 (3H, s), and 0·87 (3H, s) (Found: C, 50·0; H, 9·6; N, 7·3. $C_8H_{18}NO_2P$ requires C, 50·25; H, 9·5; N, 7·3%).

Later fractions containing an excess of the other component (δ 3·64) were crystallised from petroleum to give 2-*methoxy*-3,3,4,4-*tetramethyl*-1,2-*azaphospholidine* 2-*oxide* (21), m.p. 104—107°, M^+ 191, $\nu_{max.}$ (KBr) 3200 (NH), 1195 and 1180 (MeO·P:O), and 1035 cm^{-1} (P·OMe), δ (CCl_4) 4·85br (1H, s, NH), 3·64 (3H, d, J_{PH} 11 Hz, MeO), 3·1—2·5 (2H, m, CH_2), 1·07 (3H, d, J_{PH} 16 Hz, 3-Me), 1·06 (3H, s, 4-Me), 1·02 (3H, d, J_{PH} 16 Hz, 3-Me), and 0·97 (3H, s, 4-Me) (Found: C, 50·35; H, 9·7; N, 7·5. $C_8H_{18}NO_2P$ requires C, 50·25; H, 9·5; N, 7·3%) [yield of the mixture of (21) and (23) 3·97 mmol, 40%].

Continued elution gave a third product (0·25 g), m.p. 38—46° [from petroleum (b.p. 40—60°)–ether (8 : 3)], which could not be obtained in a pure state. It had spectroscopic properties consistent with methyl (2,2,3-trimethylbut-3-enyl)phosphonamidate (22) (1·32 mmol, 13% crude), M^+ 191, $\nu_{max.}$ (melt) 3320, 3245, and 3135 (NH_2), 1635 (C=C), 1565 (δ NH_2), 1195br (MeO·P:O), and 1035 cm^{-1} (P·OMe), δ (CCl_4) 4·80 and 4·73 (each 1H, s with unresolved fine structure, C=CH_2), 4·01br (2H, s, exchanged with D_2O, NH_2), 3·59 (3H, d, J_{PH} 11 Hz, MeO), 1·87 (2H, d, J_{PH} 18 Hz, CH_2), 1·80 (3H, s, Me·C=C), 1·25 (6H, s, Me_2C), and smaller resonances due to impurities.

1-Amino-2,2,3,3-tetramethylphosphetan 1-oxide (14) was not formed (2% would have been detected in the n.m.r. spectrum of the crude reaction product). In this experiment no 1-methoxy-2,2,3,3-tetramethylphosphetan 1-oxide (11) was isolated, but in a preliminary experiment under (apparently) similar conditions a substantial amount (*ca.* 18%) was obtained and identified by comparison (i.r., n.m.r.) with an authentic sample.

In a control experiment under the same conditions but

[17] M. J. P. Harger and M. A. Stephen, unpublished work.

without irradiation, the azide was unchanged (i.r., n.m.r.) except for the formation of some methoxyphosphetan oxide (11) (*ca.* 5% by n.m.r.).

Photolysis of 1-*Azido*-2,2,3,4,4-*pentamethylphosphetan* 1-*Oxide* (6) *in Methanol*.—The azide (2·187 g, 10·9 mmol) in methanol (50 ml) was irradiated for 44 h until N_2 evolution ceased. Evaporation of the solvent gave a pale yellow solid, δ (C_6H_6) includes 3·65 (d, J_{PH} 11 Hz), 3·62 (d, J_{PH} 11 Hz), and 3·56 (d, J_{PH} 10·5 Hz) in the approximate ratio 1 : 3 : 1.

The bulk of this material (corresponding to 10·4 mmol azide) was crystallised from petroleum to give 2-methoxy-3,3,4,5,5-pentamethyl-1,2-azaphospholidine 2-oxide (25) (0·824 g) as a mixture of geometrical isomers, m.p. 123—130°, M^+ 205, δ (C_6H_6) includes 3·65 (d, J_{PH} 11 Hz) and 3·62 (d, J_{PH} 11 Hz) (Found: C, 52·9; H, 9·7; N, 6·9. Calc. for $C_9H_{20}NO_2P$: C, 52·7; H, 9·8; N, 6·8%). The crystallisation mother liquor was chromatographed on alumina (50 g). Elution with ether containing increasing amounts (1—10%) of methanol gave a further portion of the isomers of (25) (0·461 g; total 6·26 mmol, 60%). Repeated crystallisation from ethyl acetate afforded a small sample (50 mg) of the *major isomer* of (25), m.p. 137—138°, $\nu_{max.}$ (KBr) 3170 (NH), 1235, 1215, and 1180 (MeO·P:O), and 1035 and 1020 cm^{-1} (P·OMe), δ (C_6H_6) 3·62 (3H, d, J_{PH} 11 Hz, MeO), 2·1—1·5 (1H, m, CH), 1·17 (3H, d, J_{PH} 16 Hz, 3-Me), 1·09 (6H, s, 2 × 5-Me), 1·03 (3H, d, J_{PH} 15 Hz, 3-Me), and 0·63 (3H, d, J_{PH} 7 Hz, 4-Me), δ (CCl_4) includes 5·25br (1H, d, J_{PH} *ca.* 9 Hz, exchanged with D_2O, NH). The minor isomer of (25) [δ (C_6H_6) 3·65 (J_{PH} 11 Hz, MeO)] could not be obtained in a pure state.

Continued elution gave *methyl* (1,1,2,3-*tetramethylbut*-3-*enyl*)*phosphonamidate* (26) (0·353 g, 1·72 mmol, 16%), m.p. 107—115° from petroleum–benzene (6 : 1), M^+ 205, $\nu_{max.}$ (KBr) 3330, 3250, and 3140 (NH_2), 1640 (C=C), 1570 (δ NH_2), 1210 and 1170 (MeO·P:O), and 1045 cm^{-1} (P·OMe), δ (C_6H_6) 4·87br (2H, s, $C=CH_2$), 4·13br (2H, d, J_{PH} *ca.* 5 Hz, NH_2), 3·56 (3H, d, J_{PH} 10·5 Hz, MeO), 3·2—2·5 (1H, m, CH·C=C), 1·73br (3H, s, Me·C=C), 1·33 (3H, d, J_{PH} 17 Hz, MeC·P), 1·33 (3H, d, J_{HH} 7 Hz, Me), and 1·25 (3H, d, J_{PH} 16 Hz, MeC·P) (Found: C, 52·7; H, 9·8; N, 6·7. $C_9H_{20}NO_2P$ requires C, 52·7; H, 9·8; N, 6·8%).

1-Amino-2,2,3,4,4-pentamethylphosphetan 1-oxide (15) was not isolated, but its absence from the products could not be proven by g.l.c. or n.m.r.

In a control experiment under the same conditions but without irradiation, the azide remained unchanged (i.r., n.m.r.), no 1-methoxy-2,2,3,4,4-pentamethylphosphetan 1-oxide (12) being observed (1·5% would have been detected by n.m.r.).

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