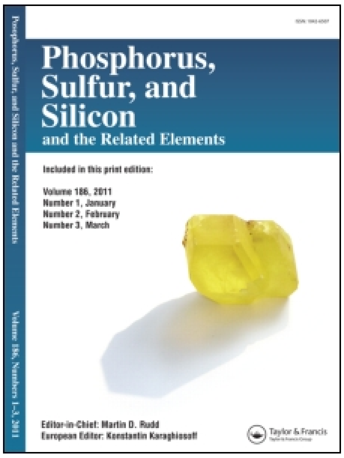

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QUASIPHOSPHONIUM INTERMEDIATES. PART V.[1] THE FORMATION OF ALKOXYPHOSPHONIUM INTERMEDIATES AND OF PHOSPHORUS-NITROGEN FISSION PRODUCTS IN REACTIONS OF NEOPENTYL *N,N,N',N'*-TETRAMETHYLPHOSPHORODIAMIDITE WITH HALOGENOMETHANES

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QUASIPHOSPHONIUM INTERMEDIATES. PART V.[1] THE FORMATION OF ALKOXYPHOSPHONIUM INTERMEDIATES AND OF PHOSPHORUS-NITROGEN FISSION PRODUCTS IN REACTIONS OF NEOPENTYL *N,N,N′,N′*-TETRAMETHYLPHOSPHORODIAMIDITE WITH HALOGENOMETHANES

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Alkoxyphosphonium halides are obtained as intermediates in the reactions of neopentyl *N,N,N′,N′*-tetramethylphosphorodiamidite with chloro-, bromo-, or iodo-methane. Whereas the iodide and bromide are well-defined crystalline solids, the chloride is low-melting and deliquescent. All are stable at room temperature and are hydrolysed only slowly. Thermal decomposition in deuterochloroform at 100°C gives neopentyl halides and methanephosphonic bisdimethylamide by S_N2-type cleavage of the alkyl-oxygen bond. The presence of moisture may give rise also to the formation of dimethylammonium salts. In reactions of the phosphorodiamidite with bromo- or chloro-methane, competing quaternization at nitrogen and the formation of trimethylamine (and hence of tetramethylammonium halides) may be correlated with increasing hardness of the halide in the order I < Br < Cl.

INTRODUCTION

Alkyl phosphorodiamidites (**1**) undergo typical Michaelis-Arbuzov reactions with a number of organic halides, although phosphorus-nitrogen fission may also occur.[2] Few examples of reactions involving simple alkyl halides have been reported[3] and the results are not entirely clear. Thus the ethyl esters (**1**, R = Et; R′ = Et or Pr^i) reacted exothermically with iodomethane to give unstable oily adducts (**2**) which yielded the corresponding alkanephosphonic diamides (**3**) on standing (Scheme 1).

$$\underset{\mathbf{1}}{(R'_2N)_2POR} \xrightarrow{R''X} \underset{\mathbf{2}}{[(R'_2N)_2P(OR)R''X]} \longrightarrow \underset{\mathbf{3}}{(R'_2N)_2P(O)R''} + RX$$

SCHEME 1

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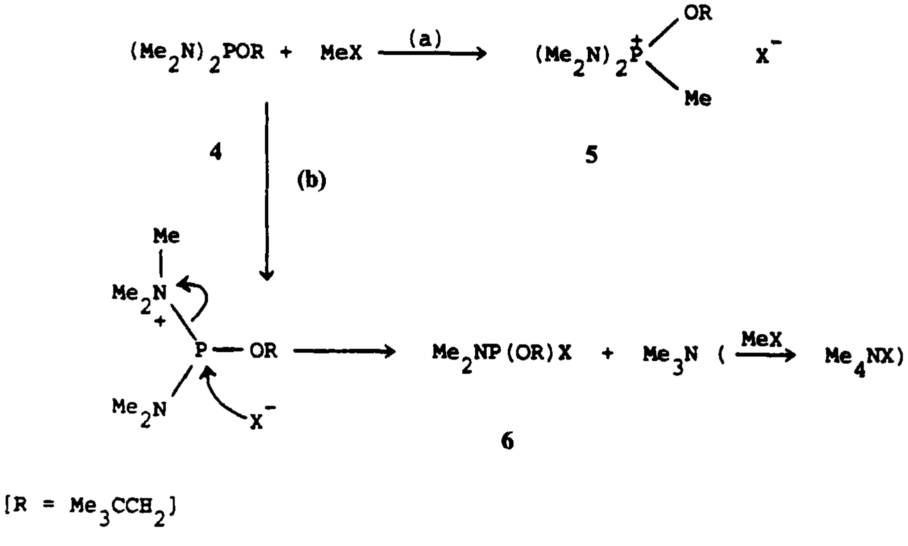
$$(Bu^i_2N)_2\overset{+}{P}(OPh)Me\ I^- \longrightarrow (Bu^i_2N)_2\overset{+}{P}MeI + OPh^-$$

$$PhO^- + MeI \longrightarrow PhOMe + I^-$$

SCHEME 2

In addition, the diethylamino derivative (**2**, R = R′ = Et) gave diethylammonium iodide. This product can only be explained, however, by the assumption that hydrogen iodide was formed, either in an elimination reaction or more probably through hydrolysis. The sensitivity of these compounds to moisture is indicated by the deliquescent nature of the crystalline piperidino derivative (**2**, R = Et, R'_2 = C_5H_{10}, R″ = Me). The only other phosphonium species reported in reactions of this type was obtained from the phenyl ester (**1**, R = Ph; R′ = Bu^i) by heating with two equivalents of iodomethane.[3] In this case the product, formulated as $(Bu^iN)_2P(Me)I_2$, was presumably formed by displacement of phenoxide by iodide from the first-formed 1 : 1 adduct, although the latter was not identified (Scheme 2). In continuation of our studies on stabilised intermediates derived from neopentyl esters,[1,4–6] we have prepared the methyl halide adducts of neopentyl *N*,*N*,*N*′,*N*′-tetramethylphosphorodiamidite (**4**) (Scheme 3, pathway *a*) and we report their properties and reactivities. In addition, the process of phosphorus-nitrogen fission has been investigated.



SCHEME 3

TABLE I

Products from the reactions of neopentyl *N,N,N',N'*-tetramethylphosphorodiamidite with halogenomethanes

X in MeX (mol. equiv.)	Reaction products (mole %)		
	$(Me_2N)_2\overset{+}{P}(OR)Me\ X^-$	$Me_2NP(OR)X^a$	Me_4NX^b
I (1–5)	100^a (80.9–100)^b	0	0
Br (2.6)	86^a (88.6)^b	14	3.9
Cl (2.5)	83^a (30.1)^b	17	10.4; 13.0^c

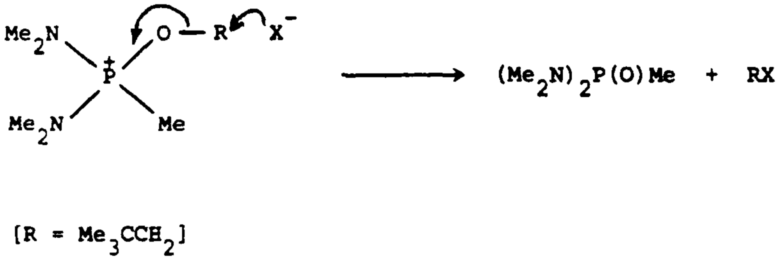
[a] Yields by ^1H n.m.r. analysis of product mixtures.
[b] Isolated yields. [c] Found: Cl, 31.6. Calc. for $C_4H_{12}ClN$: Cl, 32.4%.

RESULTS AND DISCUSSION

The reaction of neopentyl *N,N,N',N'*-tetramethylphosphorodiamidite with iodomethane in various molecular proportions (1 : 1 to 1 : 5) gave the alkoxyphosphonium iodide (**5**, X = I) as the exclusive product. The corresponding phosphonium halides (X = Br or Cl) were also the major products of reaction with bromomethane and chloromethane but an increasing tendency to quaternization at nitrogen in the order I < Br < Cl led to phosphorus-nitrogen fission (Scheme 3, pathway b) and the concomitant formation of the tetra-alkylammonium halides (Table I). This trend can be ascribed to increasing hardness in the acid character of the alkyl halide as the electronegativity of the halogen increases. The cleavage reactions involve nucleophilic displacement of trialkylamine from trivalent phosphorus by halide ion and give the alkyl phosphoramidohalidites (**6**, X = Cl or Br), which may be detected in solution by ^{31}P n.m.r. Although the ^{31}P chemical shifts of the phosphoramidohalidites are close to those of the corresponding phosphorodihalidites (**7**) and cannot be used to distinguish these species with certainty, the possible formation of the dihalidites by further cleavage (Scheme 4) was excluded in separate experiments. The proton n.m.r. spectra of these compounds are distinctive. The absence of reaction between the phosphoramidohalidites (**6**) and bromomethane or chloromethane is attributed to the electron-withdrawing effect of the halogen and to a consequent reduction in the tendency of the halidite to undergo quaternization at either phosphorus or nitrogen. Phosphorus-nitrogen cleavage in phosphorus(III) derivatives is known to occur in the presence of protic acids[8] and has been observed in certain reactions with acyl halides.[9,10] Cleavage by alkyl halides as described here has not been reported previously.

$$\underset{\mathbf{6}}{Me_2NP(OR)X} + MeX \xrightarrow{\times} \underset{\mathbf{7}}{ROPX_2} + Me_3N$$

SCHEME 4

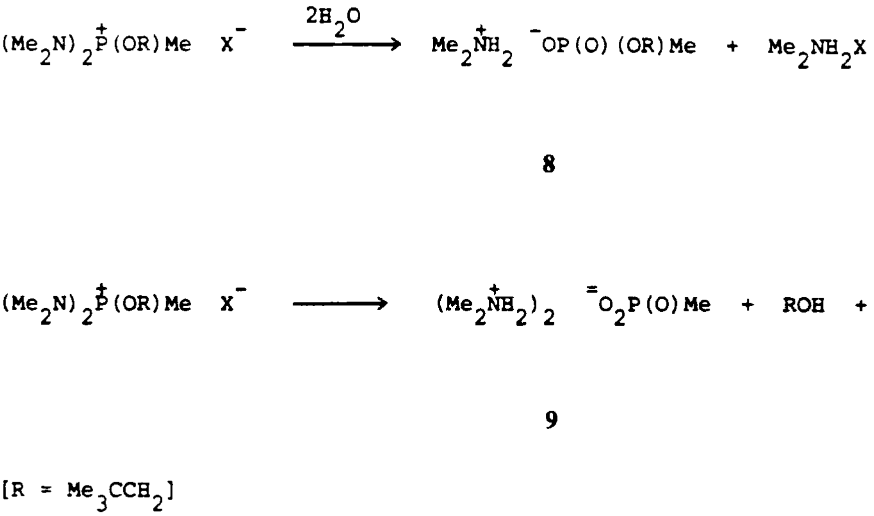


SCHEME 5

The bisdimethylamino(methyl)neopentyloxyphosphonium halides (**5**) were thermally stable and were not hydrolysed appreciably at room temperature, the bromide and iodide being well-defined crystalline solids that could be handled in the open laboratory for considerable periods of time without difficulty. The chloride, in contrast, had a relatively low melting point, was difficult to crystallise, and was highly deliquescent; nevertheless, it underwent no detectable hydrolysis in aqueous solution during several hours at room temperature. (Some hydrolysis on long standing was indicated for all halides by the development of an odour of dimethylamine during storage). ^{31}P n.m.r. spectroscopy confirmed the tetracoordinate phosphonium structure for all three compounds in solution, the chemical shifts (δ_P ca. 60 ppm) being independent of the halogen present. In solvents such as $CDCl_3$ they may be expected to exist as ion-pairs.[4,6] Thermal decomposition in deuterochloroform was negligibly slow at room temperature but occurred at 100°C to give neopentyl halides without rearrangement of the neopentyl group, indicating S_{N^2}-type cleavage of the alkyl-oxygen bond (Scheme 5). Similar results have been reported previously for a number of neopentyloxyphosphonium salts.[11] S_{N^1} cleavage and alkyl group rearrangement are observed only when strongly electron-attracting groups such as phenoxy are also attached to phosphorus.[6,12]

The diethylammonium iodide that was obtained from the iodomethane adduct of ethyl *N,N,N′,N′*-tetraethylphosphorodiamidite (**1**, R = R′ = Et), on allowing it to stand in ether,[3] was probably formed as the result of slow hydrolysis by adventitious moisture. In our present studies we found no evidence for the formation of dialkylammonium salts when water was rigorously excluded. An n.m.r. peak assignable to the dimethylammonium cation (δ_H 2.66 ppm) appeared in certain circumstances, however, during thermal decomposition in deuterochloroform and was shown to be enhanced if water was deliberately added. Under these conditions, hydrolysis of the bromide led to the formation of small but identifiable amounts of dimethylammonium bromide and the dimethylamine salts of neopentyl methanephosphonate and methanephosphonic acid (Scheme 6).

The relative importance of inductive and mesomeric effects of attached ligands in the stabilisation of alkoxyphosphonium salts has been discussed previously. For alkoxy and phenoxy ligands the inductive effect of oxygen was considered to be more important.[6] In the examples of alkoxyphosphonium salts carrying nitrogen ligands, as in the compounds referred to here and in other related cases,[13-15] the mesomeric (electron-donating) influence of nitrogen appears to be more important



$$(Me_2N)_2\overset{+}{P}(OR)Me\ \ X^- \xrightarrow{2H_2O} Me_2\overset{+}{N}H_2\ {}^-OP(O)(OR)Me + Me_2NH_2X$$

8

$$(Me_2N)_2\overset{+}{P}(OR)Me\ \ X^- \longrightarrow (Me_2\overset{+}{N}H_2)_2\ {}^{=}O_2P(O)Me + ROH + HX$$

9

$[R = Me_3CCH_2]$

SCHEME 6

in view of the stabilising effect of the dialkylamino groups. This conclusion is supported by recent X-ray diffraction studies of the iodide (**5**, X = I) which have shown the nitrogen atoms to be planar, with phosphorus-nitrogen bond lengths corresponding to significant double bond character.[16]

EXPERIMENTAL

Commercially available starting materials were used as supplied. Neopentyl phosphorodichloridite,[17] $\delta_P(CDCl_3)$ 178.3, $\delta_H(CDCl_3)$ 0.95 (s, Me_3C), 3.88 (d, CH_2O, J_{POCH} 8.4 Hz), and neopentyl phosphorodibromidite,[18] $\delta_P(CDCl_3)$ 200.4, $\delta_H(CDCl_3)$ 0.96 (s, Me_3C), 3.83 (d, CH_2O, J_{POCH} 8.4 Hz), were prepared by the methods described. ^{31}P n.m.r. spectra were recorded on a Bruker WP80 spectrometer, operating at 32.4 MHz with 85% H_3PO_4 as external standard.

Preparation of Neopentyl N,N,N′,N′-tetramethylphosphorodiamidite (**4**). Neopentyl phosphorodichloridite (11.6 g, 61.4 mmol) in petroleum ether (b.p. 30–40°C) (40 cm^3) was added dropwise and with thorough mixing (20 min) to dimethylamine (11.1 g, 247 mmol), also in light petroleum (40 cm^3) at 0°C. The mixture was allowed to warm to room temperature, dimethylammonium chloride (9.8 g, 97.5%) was removed by filtration, solvent was removed under reduced pressure, and the residual liquid was distilled to give *neopentyl N,N,N′,N′-tetramethylphosphorodiamidite* (6.4 g, 50.6%), b.p. 78–78.5°C at 12 mmHg, n_D^{20} 1.4432 (Found: P, 15.0. $C_9H_{23}N_2OP$ requires: P, 15.0%), $\delta_P(CDCl_3)$ 137.6; $\delta_H(CDCl_3)$ 0.9 (9 H, s, Me_3C), 2.5 (12 H, d, Me_2N, J_{PNCH} 8.6 Hz), 3.2 (2 H, d, CH_2O, J_{POCH} 6.3 Hz).

Preparation of Neopentyl N,N-dimethylphosphoramidochloridite (**6**; *X = Cl*). Dimethylamine (6.3 g, 140 mmol) in petroleum ether (b.p. 30–40°C) (23 cm^3) was cooled to −20°C and added dropwise with stirring (15 min) to neopentyl phosphorodichloridite (13.2 g, 69.8 mmol), also in light petroleum (47 cm^3) at −20°C. The mixture was filtered at room temperature and the filtrate was distilled after removal of solvent to give *neopentyl N,N-dimethylphosphoramidochloridite* (7.2 g, 52.3%), b.p. 44–48°C at 0.1 mmHg, n_D^{23} 1.4581 (Found: Cl, 17.8. $C_7H_{17}ClNOP$ requires Cl, 17.9%), $\delta_P(CDCl_3)$ 178.4; $\delta_H(CDCl_3)$ 0.94 (9 H, s, Me_3C), 2.66 (6 H, d, Me_2N, J_{PNCH} 12.6 Hz), 3.55 (2 H, d, CH_2O, J_{POCH} 7.2 Hz).

Preparation of Neopentyl N,N-dimethylphosphoramidobromidite (**6**, *X = Br*). Dimethylamine (7.1 g, 158 mmol) in petroleum ether (b.p. 30–40°C) (30 cm^3) was cooled to −20°C and added dropwise (20 min) to neopentyl phosphorodibromidite (21.0 g, 75.5 mmol), also in light petroleum (60 cm^3) at −20°C. Diethyl ether (50 cm^3) was added at room temperature, the mixture was filtered, and the filtrate was concentrated and distilled to give a main fraction (10.7 g) b.p. 55–63°C at 0.1 mmHg. Redistillation afforded pure *neopentyl N,N-dimethylphosphoramidobromidite* (2.8 g, 15.3%), b.p. 81–82°C at 0.3 mmHg (Found: Br, 31.6. $C_7H_{17}BrNOP$ requires: Br, 33.0%), $\delta_P(CDCl_3)$ 198.3; $\delta_H(CDCl_3)$ 0.96 (9 H, s, Me_3C), 2.64 (6 H, d, Me_2N, J_{PNCH} 13.8 Hz), 3.65 (2 H, d, CH_2O, J_{POCH} 7.2 Hz).

Reactions of Neopentyl N,N,N',N'-tetramethylphosphorodiamidite (4) *with Halogenomethanes.* (a) *Iodomethane.* Iodomethane (0.47 g, 3.3 mmol) was added to the ester (4) (0.6 g, 2.9 mmol) at room temperature. An exothermic reaction occurred with the immediate formation of a crystalline mass which was washed with ether and dried *in vacuo* to give *bisdimethylamino(methyl)neopentyloxyphosphonium iodide* (0.82 g, 80.9%) (Found: C, 34.2; H, 7.4; N, 8.4; P, 9.0. $C_{10}H_{26}IN_2OP$ requires: C, 34.5; H, 7.5; N, 8.1; P, 8.9%), m.p. 144°C, $\delta_P(CDCl_3)$ 59.6, $\delta_H(CDCl_3)$ 1.01 (9 H, s, Me_3C), 2.35 (3 H, d, CH_3P, J_{PCH} 13.8 Hz), 2.89 (12 H, d, Me_2N, J_{PNCH} 9.6 Hz), 3.91 (2 H, d, CH_2O, J_{POCH} 4.2 Hz). Identical products were obtained (3.4 g, 100%), m.p. 144°C in each case by reaction of the ester (2.0 g, 9.7 mmol), with iodomethane [(a) 2.8 g, 19.7 mmol; (b) 4.2 g, 29.6 mmol; (c) 7.0 g, 49.3 mmol].

(b) *Bromomethane.* The ester (4) (21.7 g, 105 mmol) in dry ether (20 cm^3) was added dropwise and with thorough mixing to a solution of bromomethane (10.0 g, 105 mmol) in ether at ca. 0°C. A white precipitate which formed was filtered off, washed with ether, and dried *in vacuo* to give a crystalline mixture (24.8 g) [Found: Br, 28.4. Calc. for the phosphonium bromide (5, X = Br) (23.0 g, 72.8% yield) plus Me_4NBr (1.8 g, 11.1% yield): Br, 28.4%], δ_P(DMSO-d_6) 61.5. No separation was achieved by recrystallisation from acetonitrile.

In a further experiment the ester (4) (1.7 g, 8.25 mmol) was added to bromomethane (2.0 g, 21.1 mmol) at −80°C and the mixture was allowed to stand at room temperature (22 h). After removal of the excess of bromomethane the solid residue (2.8 g) was dissolved in the minimum of $CDCl_3$ (some cloudiness remained) and shown to contain the phosphonium bromide (5, X = Br) δ_P 60.2, δ_H 1.01 (s, Me_3C), 2.44 (d, MeP, J_{PCH} 15.3 Hz), 2.93 (d, Me_2N, J_{PNCH} 10.2 Hz), 3.93 (d, CH_2O, J_{POCH} 4.8 Hz), and the phosphoramidohalidite (6, X = Br), δ_P 199.1, δ_H 3.65 (d, CH_2O, J_{POCH} 7.2 Hz) (mol ratio ca. 86 : 14). Solid which separated was washed with chloroform and ether and identified (infrared, KBr disc)[19] as tetramethylammonium bromide (0.05 g, 3.9%), m.p. > 300°C. Concentration of the filtrate followed by addition of dry ether gave white, crystalline *bisdimethylamino(methyl)neopentyloxyphosphonium bromide* (2.2 g, 88.6%), (Found: Br, 26.5; P, 10.0. $C_{10}H_{26}BrN_2OP$ requires: Br, 26.6; P, 10.3%), m.p. 122°C, $\delta_P(CDCl_3)$ 60.2, $\delta_H(CDCl_3)$ 1.01 (9 H, s, Me_3C), 2.47 (3 H, d, CH_3P, J_{PCH} 15.6 Hz), 2.92 (6 H, d, Me_2N, J_{PNCH} 9.9 Hz), 3.93 (2 H, d, CH_2O, J_{POCH} 4.8 Hz).

(c) *Chloromethane.* The ester (4) (4.0 g, 19.4 mmol) and chloromethane (2.4 g, 47.5 mmol) were mixed at −80°C, sealed in a glass tube, and allowed to stand at room temperature. After 24 h a little solid separated and a second liquid layer formed which became solid in 6 days. Excess of chloromethane was then removed to leave a white solid (5.0 g) which gave a cloudy solution in $CDCl_3$. Filtration under N_2 afforded tetramethylammonium chloride (0.22 g, 10.4%), sublm. > 360°C, which was identified by infrared (KBr disc).[19] Addition of dry ether to the filtrate gave an oily layer which remained as a liquid residue (4.3 g) after drying *in vacuo* and which contained the phosphonium chloride (5, X = Cl), δ_P 59.8, δ_H 1.00 (s, Me_3C), 2.42 (d, MeP, J_{PCH} 14.4 Hz), 2.90 (d, Me_2N, J_{PNCH} 10.8 Hz), 3.90 (d, CH_2O, J_{POCH} 4.8 Hz), and the phosphoramidochloridite (6, X = Cl), δ_P 179.2, δ_H 0.95 (s, Me_3C), 2.66 (d, Me_2N, J_{PNCH} 9.6 Hz), 3.55 (d, CH_2O) (mol ratio ca. 83 : 17). The product crystallised in 10 weeks at 0°C and was then washed with anhydrous ether (0°C) and dried *in vacuo* to give *bisdimethylamino(methyl)neopentyloxyphosphonium chloride* (1.5 g, 30.1%), m.p. 55–60°C (sealed tube) (Found: Cl, 13.5. $C_{10}H_{26}ClN_2OP$ requires: Cl, 13.8%), $\delta_P(CDCl_3)$ 60.3, $\delta_H(CDCl_3)$ 1.0 (9 H, s, Me_3C), 2.37 (3 H, d, MeP, J_{PCH} 14.7 Hz), 2.89 (6 H, d, Me_2N, J_{PNCH} 10.2 Hz), 3.86 (2 H, d, J_{POCH} 5.0 Hz).

Investigation of the Action of Halogenomethanes on N,N-dimethylphosphoramidohalidites. (a) *Chloromethane.* The phosphoramidohalidite (6, X = Cl) (2.5 g, 12.7 mmol) and chloromethane (1.7 g, 33.7 mmol) were mixed at −80°C and sealed in a glass tube. After 28 h at room temperature the tube was cooled and opened and chloromethane was allowed to escape. The residue (2.8 g) contained only the unreacted chloridite, $\delta_P(CDCl_3)$ 178.4, $\delta_H(CDCl_3)$ 0.95(s), 2.66 (d, J_{PNCH} 12.6 Hz), 3.56 (d, J_{POCH} 7.2 Hz) and a little chloromethane δ_H 2.99(s). Signals assignable to the dichloridite (7, X = Cl) were absent.

(b) *Bromomethane.* By a similar procedure the phosphoramidohalidite (6, X = Br) (1.7 g, 7.0 mmol) and bromomethane (2.0 g, 21.1 mmol), after 4 days at room temperature, gave a residue (2.1 g) containing the unreacted bromidite, $\delta_P(CDCl_3)$ 198.1, $\delta_H(CDCl_3)$ 0.97(s), 2.63 (d, J_{PNCH} 13.5 Hz), 3.64 (d, J_{POCH} 7.2 Hz) and some bromomethane, δ_H 2.63(s). No dibromidite (7, X = Br) was detectable.

Thermal Decomposition of Bisdimethylamino(methyl)neopentyloxyphosphonium Halides. (a) *In anhydrous $CDCl_3$.* Solutions of the halides (ca. 10%) in $CDCl_3$ were heated in sealed ^1H n.m.r. tubes at 100°C. In each case, decomposition gave the neopentyl halides (δ_H as reported)[18] and methylphosphonic bisdimethylamide (**8**) δ_H 1.4 (3 H, d, MeP, J_{PCH} 13.2 Hz), 2.60 (12 H, d, Me_2N, J_{PNCH} 10.8 Hz), δ_P 36.9 (lit.[20] δ_P 38.0) as follows (%/h): Cl, 60/4, 94/9.5, 99/21; Br, 80/3.5, 98/7.5, 100/13.5; I, 16/0.75, 100/19.

(b) *In the presence of water.* A solution of the phosphonium bromide (0.1 g) in $CDCl_3$ (1 cm^3) was shaken with water (0.2 cm^3) and the mixture was then heated for 44 h at 100°C (reaction complete). ^1H n.m.r. showed the presence of neopentyl bromide, δ 1.03(s), 3.27(s), methanephosphonic bisdimethylamide, δ 1.40 (d, J_{PCH} 15.0 Hz), 2.61 (d, J_{PNCH} 10.0 Hz), and the dimethylammonium ion, δ 2.57(s) (ca. 18 mole %). In two further experiments the bromide (0.58 g) was heated (44 h at 100°C) with water alone: (a) 0.06 g (2 mol. equiv.); (b) 0.12 g (4 mol. equiv.). Tube (a) formed three layers, the upper layer slowly depositing white needle-like crystals of dimethylammonium bromide δ_H ($CDCl_3$) 2.69 (6 H, s, Me), 9.56 (4 H, br s, NH_2). The middle layer was dissolved in $CDCl_3$ and treated successively with ether and acetone to give an oily liquid which crystallised in 8 weeks. The crystals were washed with ether, dried, and identified as *dimethylammonium neopentyl methanephosphonate* (**8**), m.p. 95–100°C, δ_P ($CDCl_3$) 24.0 (quartet of triplets); δ_H($CDCl_3$) 0.91 (9 H, s, Me_3C), 1.24 (3 H, d, MeP, J_{PCH} 15.9 Hz), 2.53 (6 H, s $\overset{+}{\underline{Me_2}NH_2}$), 3.45 (2 H, d, CH_2O, J_{POCH} 5.1 Hz); δ_C 11.8 (d, MeP, J_{PC} 137.3 Hz), 26.0 (s, $\underline{Me_3}C$), 32.0 (d, Me_3C, J_{POCC} 7.3 Hz), 34.5 (s, $\overset{+}{Me_2NH_2}$), 74.5 (d, CH_2O, J_{POC} 6.1 Hz). Tube (b) formed two layers from which volatiles were removed under reduced pressure. The residue was dissolved in $CDCl_3$ and treated with ether/acetone to give a first crop of crystals which were washed with ether and dried to give *bisdimethylammonium methanephosphonate* (**9**) (0.15 g), m.p. 60°C, δ_P($CDCl_3$) 23.5 (quartet); δ_H($CDCl_3$) 1.30 (3 H, d, MeP, J_{PCH} 16.2 Hz), 2.66 (12 H, s, $\overset{+}{\underline{Me_2}NH_2}$), 9.89 (4 H, br s, $\overset{+}{NH_2}$); δ_C($CDCl_3$) 14.7 (d, MeP, J_{PC} 137.9 Hz), 34.9 (s, $\overset{+}{Me_2NH_2}$). A further crop of crystals consisted of dimethylammonium neopentyl methanephosphonate (**8**), m.p. 90–100°C, with n.m.r. data as given above.

Absorption of Water by the Phosphonium Chloride (**5**; *X = Cl*). The chloride (0.18 g) was left open to the atmosphere when it absorbed water (0.033 g, 2.7 mol. equiv.) in 5 h, forming a liquid mixture. On standing in a desiccator with P_2O_5 overnight the water content fell to 0.023 g (1.9 mol. equiv.). The ^1H n.m.r. spectrum ($CDCl_3$) showed that no reaction had occurred. A signal which slowly appeared at δ 2.66 ($\overset{+}{Me_2NH_2}$) showed that ca. 27% hydrolysis occurred in the $CDCl_3$ solution in 16 weeks.

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