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THE INTERACTION OF *N,N,N',N'*-TETRAMETHYLPHOSPHORIC TRIAMIDE WITH CHLORAL:

Phosphorus-Nitrogen Fission Products and the X-Ray Crystal Structure of *N,N,N',N'*-Tetramethyl-*N''*-(2,2,2-Trichloro-1-Dimethylaminoethyl)Phosphoric Triamide

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The interaction of *N,N,N',N'*-tetramethylphosphoric triamide with chloral gives dimethylformamide, chloroform, and a complex mixture of phosphorus-containing products, amongst which *N,N,N',N'*-tetramethyl-*N''*-(2,2,2-trichloro-1-dimethylaminoethyl)phosphoric triamide was characterized by single crystal X-ray diffraction. Dimethylamino(imino)oxophosphorane is postulated as a tricoordinate phosphorus (V) by-product, which undergoes oligomerization or reaction with other components of the reaction system.

Keywords: Phosphoramidate; chloral; x-ray structure

INTRODUCTION

The reaction of diethyl phosphoramidate (1, $R^1 = R^2 = \text{EtO}$) with chloral (Scheme 1) readily gives the 1:1 adduct, diethyl *N*-(2,2,2-trichloro-1-hydroxyethyl)phosphoramidate (2, $R^1 = R^2 = \text{EtO}$),^[1] and similar adducts (3) are formed from carboxylic acid amides.^[2] Moderate yields of the phosphorodiamidate (2, $R^1 = \text{EtO}$, $R^2 = \text{Me}_2\text{N}$) were also obtained by the condensation of

*Corresponding author.

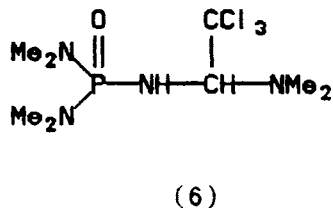
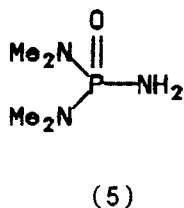
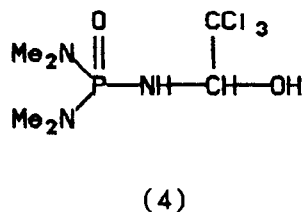
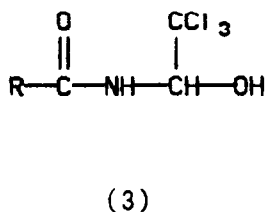


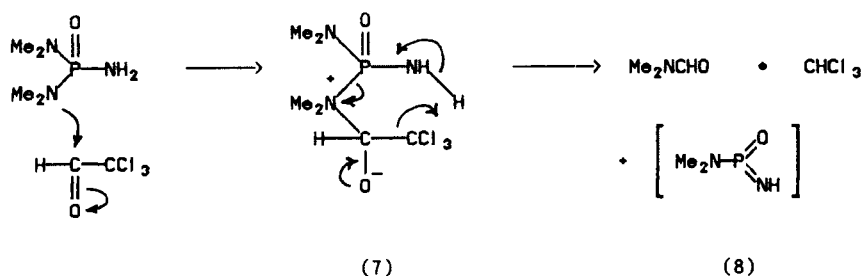
SCHEME I

ethyl *N,N*-dimethylphosphorodiamidate (1, $\text{R}^1 = \text{EtO}$, $\text{R}^2 = \text{Me}_2\text{N}$) with chloral but attempts to obtain an analogous adduct (4) from *N,N,N',N'*-tetramethylphosphoric triamide (5) were unsuccessful, as phosphorus-nitrogen fission led to a complex mixture of products.^[3]

RESULTS AND DISCUSSION

The reaction of *N,N,N',N'*-tetramethylphosphoric triamide (5) with chloral in anhydrous benzene at room temperature has been studied by nmr spectroscopy and gas chromatography and has been shown to yield dimethylformamide, chloroform, and a complex mixture of phosphorus-containing products. From the latter, *N,N,N',N'*-tetramethyl-*N''*-(2,2,2-trichloro-1-dimethylaminoethyl)phosphoric triamide (6) was isolated and characterized by single crystal X-ray dif-

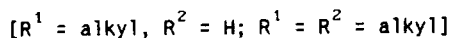
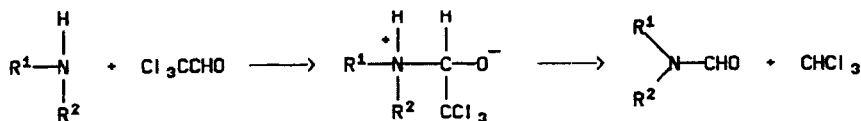




SCHEME II

fraction. The formation of polymeric phosphorus compounds was indicated by the ^{31}P nmr spectrum of resinous components of the reaction product, which showed broad and complicated signals in the regions δ_{P} 9–12, 2–9, –4 to –12, and –19 to –24 ppm.

The formation of dimethylformamide and chloroform is most reasonably explained by a reaction sequence (Scheme II) which involves nucleophilic attack of the dimethylamino nitrogen atom of the phosphoramidate (5) on chloral to give a tetrahedral intermediate (7), followed by cleavage of the phosphorus-nitrogen and carbon-carbon bonds, and proton transfer to the trichloromethyl group. Thus, collapse of the intermediate (7) to products is conveniently depicted as a concerted cyclic process, although a stepwise sequence of bond-forming and bond-breaking reactions cannot be excluded. The logical by-product in either case is dimethylamino(imino)oxophosphorane (8), a highly reactive tricoordinate phosphorus (V) species,^[4] which would be expected to undergo dimerization or oligomerization,^[5] or to react rapidly with nucleophilic components of the reaction mixture. The reactions of primary or secondary amines with chloral are also known to yield *N*-substituted formamides and chloroform (Scheme III)^[6] but in these cases no other products are formed. In the present case, the amounts of chloroform and dimethylformamide present in the reaction mixture were seen



SCHEME III

TABLE I Formation of chloroform and dimethylformamide by the interaction of *N,N,N',N'*-tetramethylphosphoric triamide (5) with chloral in benzene

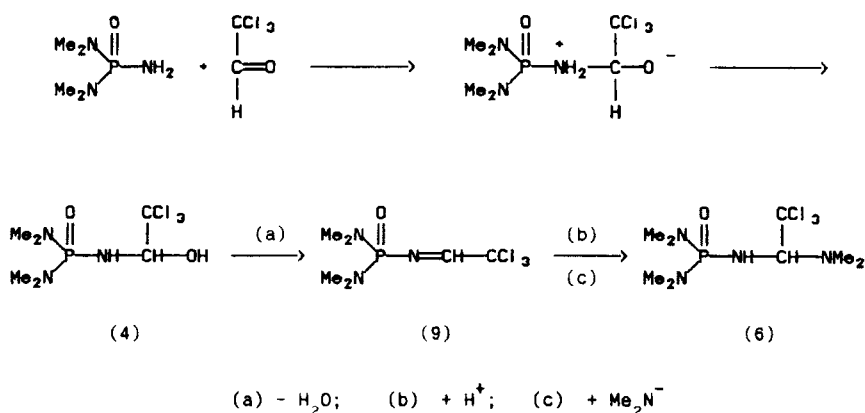
Reaction time/days	CHCl_3 (mol %) ^a	DMF (mol %) ^a
1	46	20
2	36	26
4	18	20

^aDetermined by GLC; see experimental section. Identities also confirmed by NMR: CHCl_3 , δ_{H} 7.34; DMF, δ_{H} 2.85, 2.96. (Similar to authentic samples).

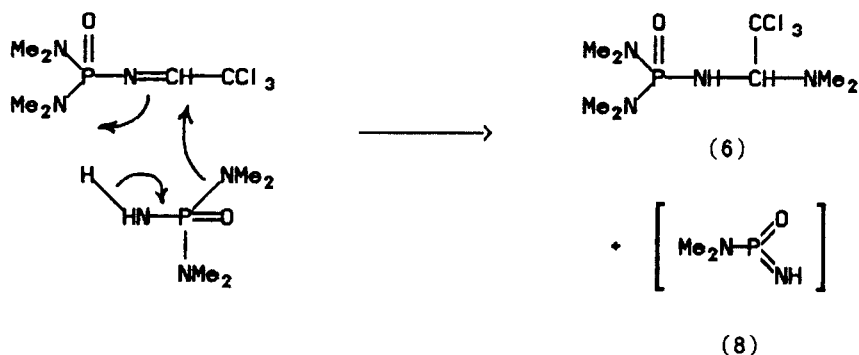
to reach a maximum and then to decrease (Table I), indicating that these products underwent further reaction after their initial formation.

Attempts to trap the intermediate (8) by carrying the reaction out in the presence of methanol were not successful; chloral reacts rapidly with methanol to form a stable hemiacetal^[7] which was unreactive towards the phosphoramidate (5).

The overall complexity of the reaction products (as evidenced by the numerous ^{31}P nmr signals observed), precluded separation and identification of individual components, except for *N,N,N',N'*-tetramethyl-*N''*-(2,2,2-trichloro-1-dimethylaminoethyl)phosphoric triamide (6), of which a small quantity was obtained as crystals and identified by X-ray diffraction and nmr spectroscopy. The formation of this unexpected product (6) indicates that nucleophilic attack by the primary amino group of the phosphoramidate (5) on chloral may lead initially to the 1:1 adduct (4), but that the latter undergoes further reaction in which the hydroxy group is replaced by dimethylamino. A possible reaction sequence (Scheme IV) involves formation of the 1:1 adduct (4), followed by the elimination of water to yield an intermediate imine (9), protonation of the imine, and



SCHEME IV



SCHEME V

transfer to the imino carbon atom of a dimethylamino group. If both the proton and the dimethylamino group originate from the same molecule of phosphoramidate (5) a concerted cyclic process may be envisaged (Scheme V), with elimination of the same tricoordinate phosphorus (V) species (8) as that shown in Scheme II. Direct substitution of the hydroxyl group of the 1:1 adduct (4) by dimethylamino is considered unlikely on steric grounds^[8] and on the basis of general mechanistic considerations.

Complete assignment of the numerous signals observed in the ^{31}P nmr spectrum of the products has not been possible, except that the singlet at *ca.* 23 ppm, which decreases in intensity as the reaction proceeds, is almost certainly due to unreacted phosphoramidate (5). The other significant singlets in this region (δ_{P} 20.4 and 20.2) are likely to be due to related species that still contain the $(\text{Me}_2\text{N})_2\text{P}(\text{O})\text{NH}-$ group, possibly the 1:1 complex (4) and the crystalline product (6). Higher field signals, of which many were observed, can be attributed to products in which fission of at least one of the P-N bonds has occurred. These signals, mainly in the region +10 to -10 ppm, but also at *ca.* -20 ppm, showed broad and complicated features, indicative of multiple coupling and the possible presence of polymeric structures.

X-Ray Crystal Structure of N,N,N',N'-tetramethyl-N''-(2,2,2-trichloro-1-dimethylaminoethyl)phosphoric triamide (6)

Principal bond lengths and bond angles for the phosphoric triamide (6) (Figure 1) are shown in Tables II and III. The phosphorus atom exhibits a distorted tetrahedral structure, with bond angles varying between $101.8(3)^\circ$ and $120.2(3)^\circ$, and having a mean value of $109.5(3)^\circ$. The phosphorus-oxygen bond length

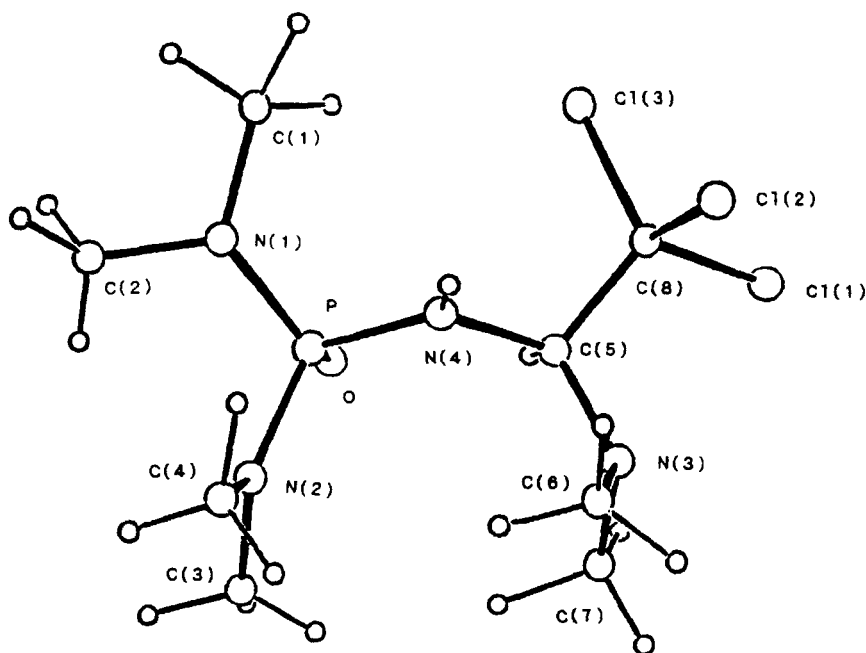


FIGURE 1 Structure of *N,N,N',N'*-tetramethyl-*N''*-(2,2,2-trichloro-1-dimethylaminoethyl)phosphoric triamide (6).

[1.498(4) Å] is longer than that reported for other phosphoryl compounds in which P-N bonds are not present, e.g. triphenylphosphine oxide (1.46 Å),^[9] tri-*o*-tolylphosphine oxide (1.473 Å),^[10] and dimethyl 1-hydroxy-2,2,2-trichloroethylphosphonate (1.426 Å).^[11] More single bond character, and a higher degree of polarization of the P=O bond, is thus indicated in the case of the phosphoric triamide (6), although the bond is still significantly shorter than the calculated length for a P-O single bond (1.76 Å).^[12] The double bond character of the phosphoryl bond in compound (6) may be reduced in comparison with that in phosphoryl compounds which contain no P-N bonds, by electron donation from

TABLE II Principal bond lengths (Å) in *N,N,N',N'*-tetramethyl-*N''*-(2,2,2-trichloro-1-dimethylaminoethyl)phosphoric triamide (6)

P-N(1)	1.647(7)	P-N(2)	1.649(6)
P-N(4)	1.645(6)	P-O	1.498(4)
N(1)-C(1)	1.436(10)	N(1)-C(2)	1.449(13)
N(2)-C(3)	1.458(10)	N(2)-C(4)	1.481(9)
N(3)-C(5)	1.459(10)	N(3)-C(6)	1.479(10)
N(3)-C(7)	1.447(10)	N(4)-C(5)	1.444(9)
C(5)-C(8)	1.558(9)	C(8)-Cl(1)	1.789(8)
C(8)-Cl(2)	1.783(7)	C(8)-Cl(3)	1.769(8)

TABLE III Principal bond angles ($^{\circ}$) in *N,N,N',N'*-tetramethyl-*N''*-(2,2,2-trichloro-1-dimethylaminoethyl)phosphoric triamide (6)

N(2)-P-N(1)	103.3(3)	N(4)-P-N(1)	101.8(3)
N(4)-P-N(2)	112.7(3)	O-P-N(1)	120.2(3)
O-P-N(2)	109.8(3)	O-P-N(4)	108.9(3)
C(1)-N(1)-P	121.9(6)	C(2)-N(1)-P	119.6(5)
C(2)-N(1)-C(1)	112.6(7)	C(3)-N(2)-P	123.3(5)
C(4)-N(2)-P	121.8(5)	C(4)-N(2)-C(3)	113.8(6)
C(6)-N(3)-C(5)	116.4(6)	C(7)-N(3)-C(5)	111.8(6)
C(7)-N(3)-C(6)	110.7(6)	C(5)-N(4)-P	120.4(4)
N(4)-C(5)-N(3)	118.2(5)	C(8)-C(5)-N(3)	108.2(6)
C(8)-C(5)-N(4)	111.3(6)	Cl(1)-C(8)-C(5)	108.6(5)
Cl(1)-C(8)-C(5)	112.8(4)	Cl(2)-C(8)-Cl(1)	107.9(4)
Cl(3)-C(8)-C(5)	111.6(5)	Cl(3)-C(8)-Cl(1)	107.5(4)
Cl(3)-C(8)-Cl(2)	108.3(4)		

the attached nitrogen atoms to phosphorus. All three P-N bond lengths are closely similar with a mean value of 1.647(6) Å; they are significantly less than that calculated for a single P-N bond (1.80 Å)^[13] but not as short as that observed (mean 1.595 Å) between the dimethylamino nitrogen atoms and positively charged phosphorus in the bisdimethylaminophosphonium salt, (Me₂N)₂P⁺(OR)Me I⁻ (R = neopentyl).^[14] Electron donation from the nitrogen lone pairs to phosphorus in compound (6) is also indicated by the bond angles at nitrogen (Σ = 354.1° and 358.9° for the two Me₂N groups), which show a close approach to planarity and sp² hybridization. In contrast, the nitrogen atom of the dimethylamino group attached to the saturated methine carbon atom is pyramidal, with a mean bond angle of 113.0(6)°.

The molecules of compound (6) form linear chains by intermolecular hydrogen-bonding between the oxygen atom of the phosphoryl group and the amido proton, with an interatomic P=O----H-N distance of 2.03 Å.

EXPERIMENTAL

N,N,N',N'-Tetramethylphosphoric triamide (5) was prepared as described.^[15] Anhydrous chloral was obtained from BDH Ltd. Benzene was dried over sodium wire.

Spectroscopy

Nmr spectra were recorded on a Bruker WP80 instrument operating at 80.02 MHz for ¹H spectra and at 32.40 MHz for ³¹P spectra. Chemical shifts are downfield relative to TMS (internal standard, for ¹H) and 85% H₃PO₄ (external standard, for ³¹P).

Gas Chromatography

Analyses were carried out on a Perkin-Elmer F11 instrument fitted with flame ionization and electron capture detectors and $2\text{ m} \times 4\text{ mm}$ o.d. glass columns. Determinations of chloroform were made using 10% Apiezon on Celite at 50°C , and of dimethylformamide using 10% EGSS-X on Celite at 120°C . Quantitative data were obtained by the method of standard addition.

Interaction of *N,N,N',N'*-tetramethylphosphoric Triamide (5) with Chloral

- (1) A solution of anhydrous chloral (0.98 g, 6.6 mmol) in benzene (10 cm^3) was added to *N,N,N',N'*-tetramethylphosphoric triamide (5) (1.0 g, 6.6 mmol), also in benzene (30 cm^3), with exclusion of moisture. After 3h, the solvent and other volatile materials were removed under reduced pressure (finally at 0.1 mmHg) and the residue was stored in a desiccator overnight. Examination of the residue by $^{31}\text{P}\{^1\text{H}\}$ nmr (CDCl_3) showed sharp singlets at δ_{P} 23.1 (starting material), 20.5, -6.8 , -9.3 , and broad complex signals centred at 11.7, 5.8, -6.6 , -7.5 , and -22 ppm.
- (2) In a similar experiment, after 3 days reaction, a resinous material separated. The clear benzene solution was removed by decantation, the solvent was removed under reduced pressure, and the residue was examined by $^{31}\text{P}\{^1\text{H}\}$ ($\text{DMSO}-d_6/\text{CDCl}_3$): sharp singlets were observed at δ_{P} 22.9, 20.4, 20.2, -0.4 , and broad complex signals centred at 10.0, 5.3, -6.5 , and -10 ppm. The resinous material, in $\text{DMSO}-d_6/\text{CDCl}_3$, showed broad signals in the regions δ_{P} 9 $-$ 12, 2 $-$ 9, -4 to -12 , and -19 to -24 , with superimposed singlets at 23.9, 20.7, 16.1, -4.0 , and -10.0 ppm.
- (3) In a third similar experiment, the solution was monitored by GLC over a period of 4 days during which chloroform and dimethylformamide were shown to be formed as shown (Table I). The clear benzene solution was then decanted from the deposit that had formed and was evaporated to leave a white resinous solid, which gave crystals from benzene and petroleum (b.p. $60\text{--}80^\circ\text{C}$) of *N,N,N',N'*-tetramethyl-*N''*-(2,2,2-trichloro-1-dimethylaminoethyl)phosphoric triamide (6) (12 mg), δ_{P} (CDCl_3) 19.7; δ_{H} (CDCl_3) 2.52 (6H, s, Me_2NCH), 2.68 and 2.72 [12H, 2 overlapping d, $^3J_{\text{PNCH}}$ 10 Hz, $(\text{Me}_2\text{N})_2\text{P}$], 2.99 (1H, m, NH), 4.70 (1H, dd, CH); structure determined by X-ray diffraction (see below).

X-Ray Crystallography

A suitable crystal of the compound (6) was obtained by crystallization from benzene/petroleum (b.p. $60\text{--}80^\circ\text{C}$). Data were collected on a Philips PW1100 diffractometer, using Mo-K_α radiation ($\lambda = 0.71069\text{ \AA}$) in the θ range $3\text{--}25^\circ$.

The structure was solved by direct methods^[16] and all hydrogen atoms were located in a subsequent difference-Fourier synthesis. All non-hydrogen atoms were assigned anisotropic thermal parameters. Refinement converged at $R = 0.0745$ and $R_w = 0.0733$ for 1640 unique reflections with $I > 3\sigma(I)$. Weights of $1/\sigma^2(F)$ were assigned to individual reflections.

Crystal Data for N,N,N',N'-tetramethyl-N''-(2,2,2-trichloro-1-dimethylaminoethyl) phosphoric triamide (6)

$C_8H_{20}Cl_3N_4OP$, $M = 324.0040$, monoclinic, space group $P2_1/n$, $a = 14.735(3)$, $b = 10.450(2)$, $c = 10.275(3)$ Å, $\beta = 101.90(3)^\circ$, $U = 1548.15$ Å³, $Z = 4$, $D_x = 1.39$ cm⁻³, $F(000) = 680$, $\mu(\text{Mo-K}\alpha) = 6.23$ cm⁻¹. Further details of atomic coordinates, bond lengths, and bond angles are deposited with the Cambridge Crystallography Data Centre.

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