

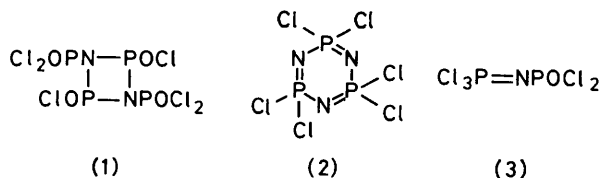
## Optimized Synthesis and Mechanism of Formation of 2,4-Dichloro-1,3-bis(dichlorophosphoryl)-2,4-dioxocyclodiphosph(v)azane from Phosphoryl Chloride and Ammonium Chloride

By Roger De Jaeger† and David R. Taylor,\* Chemistry Department, University of Manchester Institute of Science and Technology, Manchester M60 1QD

Detailed investigation of the reaction between  $[\text{NH}_4]\text{Cl}$  and an excess of  $\text{POCl}_3$  has established a procedure for isolation of the main product, the novel title cyclodiphosph(v)azane, and permitted the identification of three other reaction products, namely, pyrophosphoryl chloride, hexachlorocyclotriphosph(v)azene, and *PPP*-trichloro-*N*-dichlorophosphorylmonophosph(v)azene. A reaction mechanism is proposed which accounts for the formation of all four products.

ALTHOUGH reactions between phosphorus pentachloride and ammonia, amines, and ammonium chloride have given rise to numerous publications, including one<sup>1</sup> which discussed the increased yield of hexachlorocyclotriphosph(v)azene which results from the reaction of  $\text{PCl}_5$  with  $[\text{NH}_4]\text{Cl}$  in the presence of  $\text{POCl}_3$ , there have been relatively fewer such studies of the behaviour of phosphoryl chloride  $\text{POCl}_3$ . The reaction of  $\text{POCl}_3$  with ammonia is known to be quite complicated,<sup>2-4</sup> whereas with alkylamines the compounds arising out of the replacement of one, two, or three chlorine atoms have been isolated.<sup>5,6</sup> By contrast, Michaelis<sup>7</sup> isolated a cyclodiphosph(v)azane ( $\text{PhN}\cdot\text{POCl}_2$ ) from the reaction between aniline and  $\text{POCl}_3$  at 120 °C.

A preliminary communication about the formation of a compound with the empirical formula  $\text{P}_2\text{O}_2\text{NCl}_3$  from the reaction between a large excess of  $\text{POCl}_3$  and ammonium chloride has been reported.<sup>8</sup> The compound was provisionally identified as a novel cyclodiphosph(v)azane (1), but the parameters which control its formation proved



difficult to determine particularly because of the compound's limited thermal stability. The results described here define the optimum conditions for the isolation of pure samples of (1), and also permit a mechanism to be proposed, following the identification of three other reaction products.

### RESULTS AND DISCUSSION

A comparison of fractional distillation, molecular distillation, solvent extraction, and selective evaporation in a nitrogen stream has shown that the best procedure for the isolation of pure samples of (1) is as follows. After the essential excess of  $\text{POCl}_3$  has been carefully removed *in vacuo*, the residual oil is extracted rapidly with anhydrous light petroleum, a solvent known for its ability to

† Present address: Laboratoire de Chimie Minérale I, Université des Sciences et Techniques, Bât C8, 59650 Villeneuve d'Ascq Cedex, France.

dissolve chlorocyclophosphazenes.<sup>9</sup> The insoluble inorganic material is then subjected to selective evaporation in a current of dry inert gas at 95 °C, leaving a residue of essentially pure cyclophosph(v)azane (1).

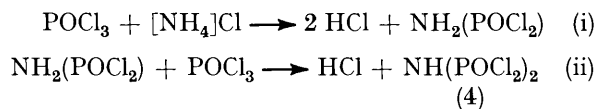
Pure samples of (1) display  $^{31}\text{P}$  n.m.r. resonances only at 9.8 and 28.0 p.p.m. The low-field signal is assigned to the  $\text{Cl}_2\text{OP}$  groups; the presence of pyrophosphoryl chloride  $\text{Cl}_2\text{OPOPOCl}_2$  in impure samples of (1) is revealed by the appearance of a shoulder on this band at *ca.* 9.5 p.p.m.<sup>10</sup> The broad high-field signal, assigned to the  $\text{N}-\text{P}(\text{O})(\text{Cl})-\text{N}$  phosphorus, is at a shift value comparable with those reported for compounds of the type  $\text{PCl}(\text{NR}_2)_2\text{O}$ .<sup>11</sup> These assignments are fully consistent with published values for other compounds also containing the  $\text{Cl}_2\text{OPNRPOCl}$  function.<sup>12,13</sup> It was not possible to obtain useful mass-spectral data for the cyclodiphosph(v)azane (1) as this compound is involatile and undergoes polycondensation on heating.

The identities of three other reaction products have now been established, following their isolation by distillation of crude samples of (1) at low pressure and at temperatures low enough to ensure that (1) does not decompose. Pyrophosphoryl chloride, already recognized from the  $^{31}\text{P}$  n.m.r. spectrum, distils out first, followed by the hexachlorocyclotriphosph(v)azene (2) and the monophosph(v)azene (3).

The cyclic phosphazene (2) may also be isolated by rapid hydrolysis of the crude product, and is easily recognized by its i.r. ( $\nu_{\text{max}}$  at 1 370, 1 310, 1 200, 880, 605, 530, and 340  $\text{cm}^{-1}$ )<sup>14</sup> and  $^{31}\text{P}$  n.m.r. spectra, the latter being a singlet at -20 p.p.m.<sup>15</sup> Similarly, the monophosphazene (3) is recognizable from its known  $^{31}\text{P}$  n.m.r. spectrum, consisting of two doublets ( $J$  *ca.* 18 Hz) at 0.05 and 13.5 p.p.m.<sup>16</sup> These compounds are not, we believe, formed by thermal decomposition of (1) during the purification, since with hindsight their presence may be discerned in crude (1) by i.r.<sup>14,17,18</sup> and verified by mass spectrometry [(2),  $m/e$  at 345 ( $\text{N}_3\text{P}_3\text{Cl}_6^+$ ) and 310 ( $\text{N}_3\text{P}_3\text{Cl}_5^+$ ); (3),  $m/e$  at 267 ( $\text{NP}_2\text{OCl}_5^+$ ), 232 ( $\text{NP}_2\text{OCl}_4^+$ ), 197 ( $\text{NP}_2\text{OCl}_3^+$ ), and 162 ( $\text{NP}_2\text{OCl}_2^+$ );  $(\text{Cl}_2\text{OP})_2\text{O}$ ,  $m/e$  at 215]. The molar proportions of the three by-products present in crude samples of (1) are indicated by the analytical data (a combination of calcination to PON, elemental analyses, and acid equivalence) to be [relative to (1) as 100%]: pyrophosphoryl chloride, 10%; the

cyclic phosphazene (2), 2%; and the monophosphazene (3), 5%. Furthermore, although one may minimize the proportion of the three impurities, their formation cannot be completely prevented, in spite of all precautions regarding the purity of the reagents and the exclusion of all traces of moisture. We therefore conclude that these compounds are genuine by-products of the formation of (1), so that any mechanism proposed for the reaction must also explain how they arise.

The first step in the reaction of  $\text{POCl}_3$  with ammonium chloride must involve nucleophilic attack upon phosphorus, producing  $\text{NH}_2(\text{POCl}_2)$  [equation (i)], and in the presence of a large excess of  $\text{POCl}_3$  a logical second step

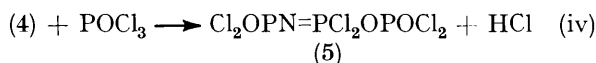


is the formation of the imine (4) [equation (ii)]. The imine (4) has previously been isolated<sup>19</sup> and was then reported to decompose on heating with evolution of HCl, suggesting the occurrence of a bimolecular condensation [equation (iii)] which would produce the main product (1) directly. Reactions similar to (iii) have been re-



ported for  $\text{NHP}(\text{POCl}_2)$ <sup>20</sup> and for compounds of the type  $\text{R}_2\text{NP}(\text{O})(\text{Cl})\text{NHR}'$  (e.g.  $\text{R} = \text{Et}$ ,  $\text{R}' = \text{Pr}^i$ ).<sup>6</sup> Work still in progress has shown that (1) is formed by the interaction of (4) with boiling  $\text{POCl}_3$ .<sup>21</sup>

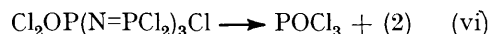
Since earlier workers tried unsuccessfully to prepare the trisubstitution product  $\text{N}(\text{POCl}_2)_3$ , we exclude the replacement of the remaining hydrogen in (4) by  $\text{POCl}_2$ , and propose instead a linear condensation to form the pyrophosphorylazene (5) [equation (iv)]. Similar reactions have been reported previously by Riesel and co-workers<sup>22</sup> and by Schmidpeter and Luber.<sup>23</sup> The key



intermediate (5) may subsequently react again with  $\text{POCl}_3$  to give two of the observed products, (3) and pyrophosphoryl chloride [equation (v)].



The remaining problem is to account for the formation of the cyclotriphosph(v)azene  $(\text{NPCL}_2)_3$ . We believe that this arises by attack of ammonium chloride upon the phosphazene (3), which is finally present in lower concentration than its concomitantly formed product, pyrophosphoryl chloride; such attack, leading to formation of  $\text{Cl}_2\text{OPN}=\text{PCl}_2(\text{NH}_2)$ , may then be followed by a sequence of steps closely analogous to equations (ii), (iv), and (v), leading finally to linear phosph(v)azenes of the type  $\text{Cl}_2\text{OP}(\text{NPCL}_2)_n\text{Cl}$  (6). The formation of (2) from (6) by elimination of  $\text{POCl}_3$  [equation (vi)], a known reaction,<sup>1,24</sup> completes the sequence.



An alternative explanation for the presence of (2) is to allow for a polycondensation of (5), formed in equation (iv), with elimination of pyrophosphoryl chloride [equation (vii)].



#### EXPERIMENTAL

All reactions and other manipulations were carried out under strictly anhydrous conditions, using a continuously purged nitrogen-filled glove-box when appropriate. Merck phosphoryl chloride was redistilled twice prior to use. The crude product (1) was obtained as described previously by refluxing ammonium chloride (concentration less than 60 g l<sup>-1</sup>) in  $\text{POCl}_3$  (b.p. 106 °C), monitoring the progress of the reaction conductimetrically.<sup>8</sup> Excess of  $\text{POCl}_3$  was then removed by evaporation at low pressure and ambient temperature, to prevent polycondensation of the desired product. A typical set of elemental analytical data for (1) is:<sup>8</sup> (Found) Cl, 51.8; N, 6.0; P, 28.1; (Calc. for  $\text{Cl}_3\text{NO}_2\text{P}_2$ ) Cl, 49.6; N, 6.5; P, 28.9%.

Infrared spectra were recorded using capillary film samples between KBr discs on a Perkin-Elmer model 621 spectrophotometer fitted with grating optics. Phosphorus-31 n.m.r. data were recorded on a Bruker WP 80 spectrometer operated at 32.37 MHz.\* Chemical shifts are cited relative to 85%  $\text{H}_3\text{PO}_4$ , positive  $\delta$  values upfield. Mass spectra were obtained using an A.E.I. MS9 double-focusing spectrometer; samples were admitted from the headspace over the liquid phase at 100 °C.

*Purification of the Cyclodiphosph(v)azene (1).*—(a) *By fractional distillation.* In a typical distillation, crude (1) (50 g) yielded: (i) a fraction (5.0 g) of b.p. 40 °C at 0.1 mmHg,† identified by i.r. and mass spectroscopy (m.s.) (*m/e* 215, <sup>35</sup> $\text{Cl}_3\text{O}_3\text{P}_2$ ) as pyrophosphoryl chloride<sup>17</sup> (Found: Cl, 55.45; P, 24.6. Calc. for  $\text{Cl}_4\text{O}_3\text{P}_2$ : Cl, 56.3; P, 24.6%) containing ca. 2% of the cyclotriphosphazene (2); (ii) a fraction boiling over the range 40–85 °C at 0.1 mmHg, which crystallized on the cold surfaces of the still and was shown by i.r. to consist of a mixture of pyrophosphoryl chloride and (2), the latter identified by i.r. and m.s. in comparison with published data;<sup>14,25</sup> (iii) a fraction with b.p. 90 °C at 0.1 mmHg and also solidifying on the cold surfaces, identified as the monophosphazene (3) [Found: Cl, 64.8; N, 5.5; P, 23.6%; *M* 267. Calc. for  $\text{Cl}_5\text{NOP}_2$ : Cl, 65.9; N, 5.2; P, 23.0%; *M* (for <sup>35</sup>Cl) 267] by i.r. spectroscopy ( $\nu_{\text{max}}$  at 770  $\text{cm}^{-1}$ );<sup>18</sup> and (iv) a viscous residue of (1) and its thermal decomposition products. Although the proportions of fractions (i)–(iii) varied from run to run, (i) was always the most important [ca. 10% w/w of (1)].

(b) *By molecular distillation.* Up to ca. 3 g of crude (1) were subjected to semimicro molecular distillation at up to 60 °C at pressures below 0.1 mmHg. Pyrophosphoryl chloride and the trimer (2), the latter in somewhat increased amounts relative to those obtained by fractional distillation, could be removed by this technique, but the monophosphazene (3) was not removed at temperatures below the onset of the thermal decomposition of (1).

(c) *By solvent extraction.* Anhydrous light petroleum (b.p. 40–60 °C) and the crude product (1) (20 : 1 v/v) were agitated at between –10 and 20 °C for periods ranging from

\* By courtesy of Mr. M. Brevard, Société Brucker.

† Throughout this paper: 1 mmHg  $\approx$  13.6  $\times$  9.8 Pa.

10 min to several days, under a dry inert atmosphere. The organic layer was then decanted off the viscous inorganic residue and evaporated to dryness. Infrared spectral analysis of the extract showed that all three impurities were removed in amounts which increased with time of extraction. Unfortunately, i.r. analysis of the residue showed that decomposition of (1) commenced prior to final removal of the impurities.

(d) *Selective evaporation.* This technique consisted of purging the crude product with extremely dry nitrogen at 95 °C for 48 h. Elemental analysis<sup>8</sup> and i.r. analysis showed (Found: Cl, 50.6; N, 7.05; P, 28.4. Calc. for  $\text{Cl}_3\text{NO}_2\text{P}_2$ ; Cl, 49.6; N, 6.5; P, 28.9%) that the residue was better than 94% pure (1). A further improvement was obtained by preceding this technique by a brief period of solvent extraction (Found: Cl, 49.9; N, 6.6; P, 28.9%). The pure material (1) had i.r. absorptions at 1 305vs, 1 265s (sh), 970w, 770w, 702w, 610vs, 562 (sh), 544 (sh), and 440w  $\text{cm}^{-1}$  (no absorption from 1 500 to 4 000  $\text{cm}^{-1}$ ), and its thermal decomposition could usually be detected by i.r. spectroscopy by the development of a new band at 490  $\text{cm}^{-1}$  [(PON)<sub>n</sub>], an increase in intensity of the bands at 1 300 and 970  $\text{cm}^{-1}$ , and diminution of the band at 610  $\text{cm}^{-1}$  (P-Cl stretch).

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