

## THE SYNTHESIS OF HIGHLY PURE OCTACHLOROCYCLOTETRA-PHOSPHAZENE $(\text{PNCI}_2)_4^+$ \*

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On the basis of literature data we prepared linear chlorophosphazenes  $(\text{PCl}_3\text{NPCl}_3)^+\text{Cl}^-$  and  $(\text{PCl}_3\text{NPCl}_2\text{NPCl}_2\text{PCl}_3)^+\text{PCl}_6^-$ , and followed the course of their amonolysis. The amonolysis of these compounds leads to the formation of cyclic chlorophosphazenes  $(\text{PNCI}_2)_n$ ,  $n = 3, 4$ . We found conditions for the preparation of the tetramer  $(\text{PNCI}_2)_4$  — octachlorocyclo-tetra-phosphazene in a pure state and in a larger amount. In principle the tetramer is formed according to the reaction  $\text{PCl}_3 + \text{Cl}_2 + \text{NH}_3$ , leading to a mixture of chlorophosphazenes  $(\text{PNCI}_2)_n$ ,  $n = 3-8$ , from which it must be isolated using various separation methods.

The synthesis of pure octachlorocyclo-tetra-phosphazene is often accompanied by various preparative difficulties due to separation procedures based on distillation, extraction or fractional crystallization of mixtures containing  $(\text{PNCI}_2)_n$ ,  $n = 3-8$ , which is obtained most commonly by the reaction  $\text{PCl}_5 + \text{NH}_4\text{Cl}$  in tetrachloro-ethane<sup>1</sup>. Therefore, Becke-Goehring<sup>2</sup> described a direct synthesis of  $(\text{PNCI}_2)_4$  in an inert solvent, such as tetrachloroethane and nitrobenzene, using linear chloro-phosphazene  $(\text{PCl}_3\text{NPCl}_3)^+\text{Cl}^-$  and ammonium chloride as starting components. The synthesis consists first in a two-hours' reaction of  $\text{P}_2\text{NCl}_7$  with ammonium chloride at 90°C and reduced pressure. After the pressure has been brought to atmospheric a further amount of  $\text{NH}_4\text{Cl}$  was added and in the second step the mixture was heated for another two hours at atmospheric pressure and 140–145°C. Then the unreacted  $\text{NH}_4\text{Cl}$  was filtered off and the solvent evaporated at 100°C. At this temperature a part of the  $(\text{PNCI}_2)_4$  formed also passed into the distillate. We found that the  $(\text{PNCI}_2)_4$  obtained in this manner still contained traces of nitro-benzene and that it could not be used, for example, for the preparation of further pure derivatives with a tetrameric cyclophosphazene skeleton. Moreover, the yields of the mentioned synthesis are not high, the reaction time is relatively long and the

\* For practical reasons and in agreement with the majority of published data on inorganic heterocyclic nitrogen-phosphorus compounds, the compounds containing the  $-\text{N}=\text{P}-$ grouping in the skeleton are called phosphazenes. According to the IUPAC nomenclature the compound  $(\text{PNX}_2)_4$ , where  $\text{X} = \text{F}, \text{Cl}, \text{Br}$ , is called 2,2,4,4,6,6,8,8-octahalogeno-1,3,5,7,2,4,6,8-tetrazatetra-phosphocine.

simultaneously formed tetramer also contains a small amount of the trimer  $(\text{PNCl}_2)_3$  – hexachlorocyclotriphosphazene. It is also slightly brown in colour. Therefore we elaborated the following modified method for the preparation of  $(\text{PNCl}_2)_4$ .

In principle it is a direct amonolysis of linear ionic chlorophosphazenes  $(\text{PCl}_3\text{NPCl}_3)^+\text{Cl}^-$ , when a pure tetramer  $(\text{PNCl}_2)_4$  is formed, and the amonolysis of  $(\text{PCl}_3\text{NPCl}_2\text{NPCl}_2\text{NPCl}_3)^+\text{PCl}_6^-$ , when only partly pure  $(\text{PNCl}_2)_4$  is obtained, which can be subsequently purified by vacuum sublimation, eliminating thus a part of  $(\text{PNCl}_2)_3$ .

### EXPERIMENTAL

*Method A:* For the preparation of  $(\text{PNCl}_2)_4$  we selected the following ratio of the reactants:  $\text{NH}_3/\text{P}_2\text{NCl}_7 = 3.5 : 1$ .  $\text{P}_2\text{NCl}_7$  (15 g), prepared according to Becke-Goehring<sup>3</sup>, and 250 cm<sup>3</sup> of tetrachloroethane were introduced under exclusion of air humidity (under nitrogen) into a 250 cm<sup>3</sup> three-neck flask provided with a stirrer and a side tube for the introduction and abduction of gases. From a pressure bottle (ampoule) gaseous ammonia (2.75 g) was introduced into the above solution for 45 min at room temperature and under vigorous stirring. During the reaction the mixture warmed up a little and a white turbidity of  $\text{NH}_4\text{Cl}$  was formed. When the reaction had subsided the mixture was heated at 90°C, but no development of HCl was observed. This started only after the reaction mixture has been heated at 140°C for 30 min. After cooling of the solution the  $\text{NH}_4\text{Cl}$  formed was filtered off and the solvent distilled off from the filtrate in a vacuum, at as low a temperature as possible. A solid material (11 g) was formed which was extracted four times with light petroleum. After evaporation of this solvent the solid residue was purified by application of a vacuum (oil pump) at 90–100°C. The yield was 5.5 g of tetramer, i.e. 51.3% of the theory. According to the Becke-Goehring's method we obtained 3.1 g of the tetramer, i.e. 32.3% of the theory, from 13.5 g of  $\text{P}_2\text{NCl}_7$  and 4.7 g of  $\text{NH}_4\text{Cl}$ .

*Method B:* Attempts were made to prepare  $(\text{PNCl}_2)_4$  on reaction of  $\text{P}_5\text{N}_3\text{Cl}_{16}$  with gaseous ammonia. The molar ratio  $\text{NH}_3/\text{P}_5\text{N}_3\text{Cl}_{16} = 7 : 1$  was selected for the reaction.

A solution of 20 g of  $\text{P}_5\text{N}_3\text{Cl}_{16}$  (prepared according to ref.<sup>3</sup>) in 300 cm<sup>3</sup> of tetrachloroethane was introduced into a 500 cm<sup>3</sup> three-neck flask provided with a stirrer and tube for introducing gases, and 3.11 g of  $\text{NH}_3$  gas were introduced into the solution for 45 min under stirring. The

TABLE I

Characteristics of  $(\text{PNCl}_2)_4$  (M.w. 463.6) prepared according to procedure A

X	Calculated %	Found %	Method	M.p., °C	
				this study	literature
Cl	61.17	61.19	A	123.9	124 (ref. <sup>5</sup> )
N	12.08	11.94	B	119 <sup>a</sup> , 123 <sup>b</sup>	123.5 (ref. <sup>6</sup> )
P	26.73	26.80	C <sup>c</sup>	121	122 (ref. <sup>2</sup> )

<sup>a</sup> Before sublimation; <sup>b</sup> after sublimation; <sup>c</sup> the method according to ref.<sup>2</sup>.

reaction mixture was then heated at 140°C for 30 min. At the beginning of the heating a weak development of HCl was observed. The  $\text{NH}_4\text{Cl}$  formed was filtered off and the solvent was distilled off under reduced pressure. The solid residue was extracted 4 times with light petroleum. The tetramer obtained after evaporation of the solvent was purified by vacuum sublimation at 90–100°C in order to eliminate the traces of  $(\text{PNCl}_2)_3$ . The yield was 6.3 g (52.0%) of the product.

Characteristic of  $(\text{PNCl}_2)_4$  obtained by all three methods are summarized in Table I.

## RESULTS

The purity of the tetramer was tested by thin-layer chromatography<sup>4</sup>, melting point determination<sup>5,6</sup>, IR spectroscopy<sup>7</sup>, and <sup>31</sup>P NMR spectroscopy<sup>1</sup>. The literature value of the chemical shift for  $(\text{PNCl}_2)_4$  is  $\delta -7.4$ , while the value found by us was  $\delta -7.2$ . At the same time the powder diagram of the tetramer was compared with that from literature<sup>8</sup>.

According to TLC the product from procedure A always gave only a single spot, while the product from procedure B and the procedure according to Becke-Goehring also contained  $(\text{PNCl}_2)_3$ .

Hence, procedure A is the most suitable for the preparation of  $(\text{PNCl}_2)_4$ , because it is rapid and affords a tetramer of the required purity.

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