Phosphorus–Nitrogen Compounds. Part XL.[1] The Hydrogen Halide-induced Deaminolysis of Hexakisdimethylaminocyclotriphosphazatriene and the *cis–trans*-Isomerisation of Halogenodimethylaminocyclotriphosphazatrienes

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The reaction of hexakisdimethylaminocyclotriphosphazatriene, $N_3P_3(NMe_2)_6$, with hydrogen chloride in boiling xylene gives *cis*-$N_3P_3Cl_2(NMe_2)_4$, *cis*- and *trans*-$N_3P_3Cl_3(NMe_2)_3$. The analogous reaction with hydrogen bromide proceeds faster, gives low yields of similar products, but is accompanied by extensive decomposition. With hydrogen iodide only $N_3P_3(NMe_2)_6$,HX (X = I or I_3) are isolated. *cis*- and *trans*-Derivatives of $N_3P_3X_3(NMe_2)_3$ and $N_3P_3X_4(NMe_2)_2$ (X = Cl or Br) can be reversibly isomerised with the appropriate hydrogen halide. The mechanisms of the above reactions are discussed.

EXTENSIVE and detailed studies on the aminolysis of hexachlorocyclotriphosphazatriene, $N_3P_3Cl_6$ (1), with a variety of amines have been reported.[2] Aminolysis reactions of the corresponding hexabromide, $N_3P_3Br_6$ (2), are less well documented.[2] We describe here the deaminolysis reactions of hexakisdimethylaminocyclotriphosphazatriene, $N_3P_3(NMe_2)_6$ (3), by means of hydrogen halides. A preliminary report has appeared.[3]

On passing hydrogen chloride into solutions of the hexa-amide (3) in boiling xylene for brief periods (1 h), the monohydrochloride, $N_3P_3(NMe_2)_6{\cdot}HCl$ (4), is obtained and no appreciable deaminolysis is observed. However, on prolonging the reaction times, gradual replacement of the amino-groups by chlorine atoms takes place.

$$N_3P_3(NMe_2)_6 + 2n\mathrm{HCl} \longrightarrow N_3P_3Cl_n(NMe_2)_{6-n} + n\mathrm{Me_2NH{\cdot}HCl} \quad (n = 2 \text{ or } 3)$$

In a typical reaction (24 h), the following pure compounds are isolated by column chromatography: *cis*-$N_3P_3Cl_3(NMe_2)_3$, m.p. 152 °C (5), *trans*-$N_3P_3Cl_3(NMe_2)_3$, m.p. 105 °C (6), and *cis*-$N_3P_3Cl_2(NMe_2)_4$, m.p. 104 °C (7). The ratio of the products is *ca.* 1 : 2 : 20. The course of the reaction is conveniently followed by monitoring with t.l.c. The deamination products are formed in the order (7), (6), (5), although it is feasible that compound (5) is not a primary reaction product but that it is formed by the hydrogen chloride-catalysed isomerisation of compound (6). The observation that the *cis*-compound (5) does not appear in the reaction mixture until substantial amounts of the *trans*-compound (6) have accumulated supports this contention. Also, an independent experiment indicates that a solution of the pure *trans*-isomer (6) in boiling xylene is slowly isomerised on treatment with hydrogen chloride (see below). There is no indication from thin-layer chromatography of the formation of either *trans*-$N_3P_3Cl_2(NMe_2)_4$, or the unstable pentakisdimethylamino-compound, $N_3P_3Cl(NMe_2)_5$, which have been isolated recently from the reaction of the hexachloride (1) with dimethylamine.[4] Bis- and mono-dimethylamino-compounds are not detected even after lengthy reaction times (90 h). The relative amounts of the three deaminolysis products (5)—(7) vary with reaction time and, as anticipated, the isomers (5) and (6) increase at the expense of compound (7) [*e.g.* after 90 h only a trace of compound (7) is detected—see Experimental section].

The general pattern of the reaction of hexakisdimethylaminocyclotriphosphazatriene (3) with hydrogen bromide is analogous to that observed with hydrogen chloride. The initial product of the reaction in boiling xylene (1 h) is the monohydrobromide, $N_3P_3(NMe_2)_6{\cdot}HBr$ (8). When the reaction time is increased (3 h), gradual replacement of the amino-groups by bromine atoms occurs. Two pure compounds are isolated, *cis*-$N_3P_3Br_3(NMe_2)_3$, m.p. 170—172 °C (9) and *trans*-$N_3P_3Br_3(NMe_2)_3$, m.p. 120—121 °C (10). A third compound [t.l.c. comparison suggests a tetrakis-compound, $N_3P_3Br_2(NMe_2)_4$, (11)], was present in very small amounts but was not obtained

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in a pure state. It is interesting to note that neither $N_3P_3Br_2(NMe_2)_4$ (11), nor *cis*-$N_3P_3Br_3(NMe_2)_3$ (9), have been isolated in the dimethylaminolysis of $N_3P_3Br_6$ (2).[5]

Increase of the reaction time (>3 h) leads to extensive decomposition and the amount of deaminolysed products is drastically reduced. A t.l.c. investigation of a 4 h reaction indicates only one major compound, *trans*-$N_3P_3Br_3(NMe_2)_3$ (10), and traces of its *cis*-isomer (9). This observation suggests a much higher stability of the *trans*-trisdimethylamino-derivative (10), under these conditions compared to its *cis*-isomer (9). Decomposition has also been observed on treatment of dimethylaminofluorocyclotriphosphazatrienes with hydrogen bromide but not with hydrogen chloride.[6]

Attempts to prepare the dibromotetrakisdimethylamino-derivative, $N_3P_3Br_2(NMe_2)_4$ (11), in greater amounts by modifying the reaction conditions were not successful. T.l.c. evidence suggests that this compound is always formed, but is quickly converted into the trisdimethylamino-derivatives (9) and (10).

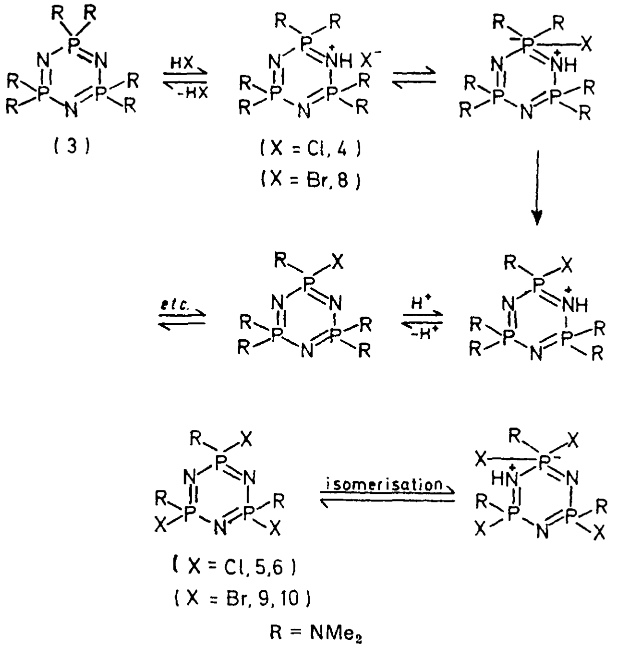
As in the case of the hydrogen chloride reactions, there is no indication of the formation of any mono- or bisdimethylaminobromo-derivatives. Although the actual deaminolysis occurs more readily with hydrogen bromide than with hydrogen chloride (an observation also made by others [6]), the ready decomposition of the dimethylaminobromo-compounds under the reaction conditions employed results in very poor yields.

When hexakisdimethylaminocyclotriphosphazatriene, $N_3P_3(NMe_2)_6$ (3), is treated with hydrogen iodide in boiling xylene solution for a short period, the product obtained initially is the monohydroiodide, $N_3P_3(NMe_2)_6 \cdot HI$ (12), m.p. 220—222 °C. When the reaction time is extended to *ca.* 1 h, hexakisdimethylaminocyclotriphosphazatriene hydrotri-iodide, $N_3P_3(NMe_2)_6HI_3$ (13), m.p. 144—145 °C, is also obtained. No deaminolysis products are detected in any experiments. If iodophosphazenes are formed, it is probable that they are too unstable to be isolated under the reaction conditions used.

Whereas deaminolysis did not proceed under our reaction conditions beyond the trishalogeno-derivatives, (5), (6), (9), and (10), it could be shown in independent experiments that the above four compounds, as well as the bisamino-derivatives, *cis*-$N_3P_3Cl_4(NMe_2)_2$, m.p. 86 °C (14), and *trans*-$N_3P_3Cl_4(NMe_2)_2$, m.p. 103 °C (15), isomerised reversibly to their geometric isomers when treated with the appropriate hydrogen halide in boiling xylene.

Replacement of amino-groups from hexakisdimethylaminocyclotriphosphazatriene, $N_3P_3(NMe_2)_6$ (3), by hydrogen halides may be regarded as proceeding through a nucleophilic attack at phosphorus by the halide ions. In a fully aminolysed cyclophosphazene the electrophilic character of the phosphorus atoms is reduced by electron-delocalisation from adjacent dimethylamino-groups; attack by nucleophiles may also be made more difficult by steric effects. A consequence of this transfer of charge is that compound (3) is a fairly strong base, $\mathrm{p}K'_{a,1}$ +7·5.[7] On protonation of a ring nitrogen atom the electron distribution in the molecule becomes modified. Protonation of a ring nitrogen atom will drain electron-density from the phosphorus atoms, especially the adjacent ones, and make them much more susceptible to nucleophilic attack by halide ions, leading to the displacement of amino-groups (deaminolysis) or halogen atoms (isomerisation). Profound structural alterations on protonation of aminophosphazenes have been observed by *X*-ray crystallography.[8] The products of deaminolysis of compound (3) by hydrogen chloride closely resemble the products (as detected by t.l.c.) of dimethylaminolysis of the hexachloride (1) [9] with one exception: dimethylaminolysis gives the geminal tris-derivative, $N_3P_3Cl_3(NMe_2)_3$, m.p. 71 °C, in comparable yields to the *trans*-isomer (6), whereas in the hydrogen chloride-induced deaminolysis its presence has not been detected.

The hydrogen halide-induced deaminolysis and isomerisation reactions can be rationalised by means of the known basicities ($\mathrm{p}K'_{a,1}$) in nitrobenzene towards perchloric acid of the above compounds, $N_3P_3Cl_{6-n}(NMe_2)_n$.[10] The basicities of the compounds diminish considerably as the number of dimethylamino-groups decreases. Also, the isomer which possesses the largest number of NMe_2 groups on phosphorus atoms α to a given ring nitrogen atom has the highest $\mathrm{p}K'_{a,1}$ value and *that* ring nitrogen atom is the preferred site of protonation. This observation, together with the halide ion X^- being a better



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leaving group than the amide ion Me_2N^-, accounts for the experimental observations. The scheme summarises these admittedly simplified rationalisations.

The decreased electron availability which occurs with decreasing number of amino-groups in the series, $N_3P_3Cl_{6-n}(NMe_2)_n$, is likely to determine the behaviour of these compounds in the three ways: (i) a decreased tendency to protonate the ring nitrogen atoms; (ii) an increased electrophilicity of the phosphorus atoms; and (iii) a much smaller tendency for a leaving group to depart. For the tris-, $N_3P_3X_3(NMe_2)_3$ (X = Cl or Br), and bis-amino-derivatives, $N_3P_3X_4(NMe_2)_2$ (X = Cl), apparently only the better leaving group (the halide ion) is able to depart. Thus, the isomerisations reported here resemble in part the two previously reported types of *cis–trans*-isomerisation.[11,12]

TABLE

Compound			Hydrogen halide	Xylene[a] (in ml)	Reaction time (t/h)	Phosphazene		
							Yield	
No.	g	mol				Product	g	%
(3)	2	0·005	HCl	100	1	(4)[b]	1·52	69
(3)	10	0·025	HCl	30	24	(5) (6) (7)	0·045 0·075 0·87	1·2 2·1 24·6
(3)	10	0·025	HCl	30	90	(5) (6) (7)	0·24 1·14 Trace[d]	7·2 34·2
(3)	5	0·0125	HCl	200[c]	20	(4)	2·63	48·2
(6)	0·2	0·0005	HCl	5	10	(5) (6)	*d* *d*	50 50
(3)	5	0·0125	HBr	150	4	(10) (9)	0·12 Trace[d]	
(3)	2	0·005	HBr	50	0·2	(8)[e]	1·9	79·2
(3)	2	0·005	HBr	20	0·5 or 1	(9) (10) (11)	Trace	
(3)	5	0·0125	HBr	15[f]	8	(9) (10) (8)	*d* *d* 0·6	
(3)	2	0·005	HBr	25	1·5	(9) (10)	0·25 0·5	9·5 19
(10)	0·2	0·0004	HBr	5	1	(9) (10)	*d* *d*	
(3)	1	0·0025	HI	150	0·2	(12)[g]	1·1	83
(3)	2	0·005	HI	30	1	(13)[h]	0·012	0·3

[a] Reflux temp. [b] M.p. 198—200 °C; Found: C, 33·4; H, 8·5; N, 28·8; Cl, 8·1. $C_{12}H_{37}ClN_9P_3$ requires C, 33·1; H, 8·5; N, 28·9; Cl, 8·15%. [c] MeCN; further heating gave no deamination. [d] Visual estimate of quantity from t.l.c. [e] M.p. 216—217 °C; Found: C, 30·5; H, 7·7; Br, 16·8. $C_{12}H_{37}BrN_9P_3$ requires C, 30·0; H, 7·7; Br, 16·7%. [f] Sealed tube 155 °C. [g] M.p. 220—222 °C; Found: C, 27·2; H, 7·2; I, 24·5. $C_{12}H_{37}IN_9P_3$ requires C, 27·3; H, 7·1; I, 24·1%. [h] M.p. 144—145 °C; Found: C, 18·5; H, 4·8; N, 16·3; I, 48·7. $C_{12}H_{37}I_3N_9P_3$ requires C, 18·5; H, 4·8; N, 16·1; I, 48·7%.

Deamination reactions of dimethylaminofluorocyclotriphosphazatrienes, $N_3P_3F_{6-n}(NMe_2)_n$ (n = 1, 2, 3, or 4), with hydrogen chloride and hydrogen bromide, to give the corresponding mixed halides, $N_3P_3F_{6-n}X_n$ (X = Cl or Br), have been reported.[6,13-15] In contrast, no deamination of the pentachlorodimethylaminocyclotriphosphazatriene, $N_3P_3Cl_5NMe_2$, was observed (g.l.c.) with hydrogen chloride after 24 h at 140 or 185 °C (*i.e.* in xylene or nitrobenzene). The pentafluoride, $N_3P_3F_5$-NMe_2, deaminates with hydrogen halides under conditions where the corresponding pentachloride, $N_3P_3Cl_5$-NMe_2, is stable, suggesting that hydrogen-bonding of the hydrogen halide to the fluorine atoms (possibly the one geminal to the dimethylamino-group), plays an important role. A related hydrogen-bonding mechanism has recently been put forward to explain the differing replacement patterns of the hexachloride (1) with different primary amines.[16]

Although the major species present in solution need not be the most reactive ones (and hence exocyclic protonation preceding deamination cannot be definitely excluded), the reaction scheme outlined in this paper seems, in the light of present evidence, to be the most likely one.

EXPERIMENTAL

Hexakisdimethylaminocyclotriphosphazatriene was prepared by the literature method.[9] One experiment is described in detail, and the remainder are summarised in the Table. Yields refer to pure products obtained after separation by column chromatography on silica. Structural assignments for compounds (5), (6), (7), (9), and (10), have been discussed previously.[9]

Preparation of Isomeric Tribromotrisdimethylaminocyclotriphosphazatrienes (cis *and* trans).—Hexakisdimethylaminocyclotriphosphazatriene (5 g, 0·0125 mol) was dissolved in freshly distilled xylene (25 ml) and hydrogen bromide was bubbled through the refluxing solution (140 °C) for 3 h. A colourless solid was precipitated initially, which gradually turned brown. The xylene solution was evaporated to dry-

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ness under reduced pressure to give an oil which on extraction with light petroleum (150 ml) gave a small amount of solid (0·25 g). T.l.c. showed two major spots along with a very faint one. Fractional crystallisation of the products gave pure crystals of the following: (i) 2-*cis*-4-*cis*-6-tribromo-2,4,6-trisdimethylaminocyclotriphosphazatriene, $N_3P_3Br_3(NMe_2)_3$ (9), m.p. 170—172 °C (0·054 g, 0·85%) (Found: C, 14·4; H, 3·95; N, 16·35; Br, 47·7. $C_6H_{18}Br_3N_6P_3$ requires C, 14·2; H, 3·8; N, 16·6; Br, 47·4%); (ii) 2-*trans*-4,6-tribromo-2,4,6-trisdimethylaminocyclotriphosphazatriene, $N_3P_3Br_3(NMe_2)_3$ (10), m.p. 120—121 °C (0·082 g, 1·3%) (Found: C, 14·5; H, 3·8; N, 16·6; Br, 47·4%).

The R_F values of the above compounds were very similar to the corresponding chloro-compounds (5) and (6). The remaining faint spot had a similar R_F value to $N_3P_3Cl_2(NMe_2)_4$ (7) and is probably the dibromotetrakisdimethylaminocyclotriphosphazatriene, $N_3P_3Br_2(NMe_2)_4$ (11). This was not separated owing to its very small amount.

The insoluble reaction product was extracted with chloroform and an i.r. spectrum indicated the presence of dimethylammonium bromide and hexakisdimethylaminocyclotriphosphazatriene hydrobromides.

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