923. *Phosphorus–Nitrogen Compounds. Part XVI.*[1] *The Reactions of Hexachlorocyclotriphosphazatriene with t-Butylamine*

By S. K. Das, R. Keat, R. A. Shaw, and B. C. Smith

t-Butylamine reacts with hexachlorocyclotriphosphazatriene to give mono-, 2,2-bis-, 2,2,4,4-tetrakis-, and hexakis-t-butylamino-derivatives, $N_3P_3Cl_{6-n}(NHBu^t)_n$ (n = 1, 2, 4, and 6). A geminal reaction pattern is established by the preparation of a series of t-butylaminodimethylamino-cyclotriphosphazatrienes. Possible reaction mechanisms are discussed.

Hexachlorocyclotriphosphazatriene reacts with primary and secondary amines to give aminocyclotriphosphazatrienes and amine hydrochlorides.[2]

$$N_3P_3Cl_6 + 2n\text{NHRR}' \longrightarrow N_3P_3Cl_{6-n}(\text{NRR}')_n + n\text{NH}_2\text{RR}'\text{Cl}$$

In Part I of this Series[3] it was reported that reaction with an excess of t-butylamine in boiling ether causes the replacement of four chlorine atoms, and it is shown here that the complete replacement of six chlorine atoms occurs under suitable reaction conditions. The hexakis-t-butylamino- and hexakisdimethylamino-cyclotriphosphazatrienes are relatively strong bases having $pK'_{a,1}$ values in nitrobenzene defined elsewhere,[4] of 8·0 and 7·6, respectively. The $pK'_{a,1}$ values of all known hexakisalkylamino-derivatives fall within the comparatively narrow range 7·6—8·8. The tetrakis-t-butylamino-derivative reported earlier,[3] $pK'_{a,1}$ 4·35, is considerably more basic than the nongeminal tetrakisdimethylamino-derivative, $pK'_{a,1}$ −1·40, which suggested the possibility of a geminal configuration for the former, because 2,2,4,4-tetra-amino-derivatives are expected to be stronger bases than 2,2,4,6-tetra-amino-derivatives.[4] A detailed investigation of the reactions of hexachlorocyclotriphosphazatriene with t-butylamine was therefore carried out, and a series of mixed t-butylamino-dimethylamino-derivatives has also been prepared to help to elucidate their structures and hence the reaction pattern. The results of the investigation are reported here.

The t-butylaminocyclotriphosphazatrienes described in this Paper are listed in Table 1. All the compounds except the hydrochlorides, which tend to sublime, have sharp melting

Table 1

Substituted cyclotriphosphazatrienes

	Substituents						
	2	2	4	4	6	6	M. p.
(I)	Cl	Cl	Cl	Cl	Cl	Cl	114°
(II)	Cl	Cl	Cl	Cl	Cl	$NHBu^t$	−10 to −11
(III)	Cl	Cl	Cl	Cl	$NHBu^t$	$NHBu^t$	120—122
(IV)	Cl	Cl	$NHBu^t$	$NHBu^t$	$NHBu^t$	$NHBu^t$	156
(V)			Hydrochloride of (IV)				295 (decomp.)
(VI)	$NHBu^t$	$NHBu^t$	$NHBu^t$	$NHBu^t$	$NHBu^t$	$NHBu^t$	280—282
(VII)	NMe_2	NMe_2	$NHBu^t$	$NHBu^t$	$NHBu^t$	$NHBu^t$	67
(VIII)			Hydrochloride of (VII)				259
(IX) *	NMe_2	$NHBu^t$	NMe_2	$NHBu^t$	$NHBu^t$	$NHBu^t$	106
(X) *			Hydrochloride				243
(XI) †			Hydrochloride				240
(XII)	NMe_2	NMe_2	NMe_2	NMe_2	$NHBu^t$	$NHBu^t$	72
(XIII) ‡	NMe_2	NMe_2	NMe_2	$NHBu^t$	NMe_2	$NHBu^t$	b.p. 110°/0·001 m.m.

* Prepared from the tetrachlorobisdimethylamino-compound (XV) of m. p. 103°. † Prepared from the tetrachlorobisdimethylamino-compound (XVI) of m. p. 86°. ‡ Prepared from the dichlorotetrakisdimethylamino-compound (XVII) of m. p. 104°.

[1] Part XV, R. Keat and R. A. Shaw, *J.*, 1965, 4802.
[2] R. A. Shaw, B. W. Fitzsimmons, and B. C. Smith, *Chem. Rev.*, 1962, **62**, 247.
[3] S. K. Ray and R. A. Shaw, *J.*, 1961, 872.
[4] D. Feakins, W. A. Last, and R. A. Shaw, *Chem. and Ind.*, 1962, 510; *J.*, 1964, 2387, 4464; and unpublished results.

points, and this, together with thin-layer chromatographic examination showing the presence of only one spot in each case, indicates that all are pure compounds and not mixtures of isomers.

The methylamino- and amino-chlorocyclotriphosphazatrienes are relatively unstable thermally,[5] in contrast to the corresponding t-butylamino- and isopropylaminochloro-derivatives, which can frequently be distilled or sublimed.

Reaction of hexachlorocyclotriphosphazatriene (I) with t-butylamine (2 moles) in boiling benzene gives a mixture of the mono- (II) and bis-derivatives (III) and unchanged starting material (I). Reaction with t-butylamine (4 moles) in boiling benzene gives an almost quantitative yield of the bis-derivative (III), whereas reaction with t-butylamine (4 moles) in boiling chloroform gives a mixture of the mono- (II), bis- (III), and tetrakis-derivatives (IV) and some unchanged starting material (I). Reaction with t-butylamine (6 moles) in boiling benzene gives an oil, which crystallises slowly to a colourless solid, m. p. 110—125°. Chromatographic separation gives the bis- (III) and tetrakis-derivatives (IV). The same products are obtained from reaction in ether. No trace of a tris-t-butylamino-derivative could be detected. Reaction of the bis-derivative (III) with t-butylamine (1·5 or 2 moles) in boiling benzene, chloroform, or ether gives again a mixture of the bis- (III) and tetrakis-derivatives (IV). Reaction of hexachlorocyclotriphosphazatriene with an excess of t-butylamine in boiling benzene gives high yields of the tetrakis-derivative (IV) and a small quantity of its hydrochloride (V). Reaction of tetrakis-t-butylamino-dichlorocyclotriphosphazatriene (IV) with an excess of t-butylamine in toluene in a sealed tube at 165° gives high yields of hexakis-t-butylaminocyclotriphosphazatriene (VI).

The absence of a tris-t-butylaminotrichlorocyclotriphosphazatriene appears significant in view of the existence of a number of triaminotrichloro-compounds, such as $N_3P_3Cl_3(NMe_2)_3$, $N_3P_3Cl_3(NEt_2)_3$, and $N_3P_3Cl_3(NH_2)_2(NMe_2)$.[2,6] Pentakis-t-butylaminochlorocyclotriphosphazatriene was not observed, and possible explanations for the absence of penta-amino-chloro-derivatives are discussed elsewhere.[6,7]

Two different replacement patterns, geminal and non-geminal, have been considered in the progressive replacement of chlorine in hexachlorocyclotriphosphazatriene.[2,3] The differences depend on whether successive replacement of chlorine atoms occurs preferentially at the same, or at different, phosphorus atoms. Reactions with dimethylamine,[6] piperidine,[8] and possibly methylamine,[9] and ammonia [9] are predominantly nongeminal. It has been suggested that reactions with strong bases (alkylamines, ammonia) follow a nongeminal pattern and that reactions with weak bases (arylamines) follow a geminal pattern,[9] but this, and an argument on which an earlier assignment of the structure of the tetrakis-t-butylamino-derivative (IV) was based,[3] are believed to be oversimplifications.

One mono-, and only one bis- and one tetrakis-t-butylamino-derivative have been prepared. This behaviour, which is very much simpler than that in the dimethylamino- [6] and piperidino [8]-systems, suggests that the replacement pattern with t-butylamine is either geminal or nongeminal under the conditions investigated, and not a mixture of both. Furthermore, if it is nongeminal the reactions must be stereospecific.

Chemical evidence for the geminal configuration of the tetrakis-t-butylamino-derivative (IV) depends on its reaction with an excess of dimethylamine to give the hydrochloride (VIII), identical with the product obtained by reaction of the geminal bisdimethylamino-derivative,[6] $N_3P_3Cl_4(NMe_2)_2$, m. p. 62° (XIV), with an excess of t-butylamine in benzene, in a sealed tube at 130°. Removal of the hydrogen chloride with a stoicheiometric quantity of potassium hydroxide in ethanol gives the free base (VII).

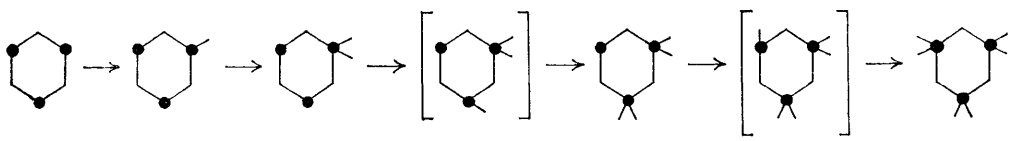
There are three possible isomers of composition $N_3P_3(NMe_2)_2(NHBu^t)_4$ (neglecting the

[5] R. Keat, S. K. Ray, and R. A. Shaw, unpublished results.
[6] R. Keat and R. A. Shaw, *J.*, 1965, 2215.
[7] K. Hills and R. A. Shaw, *J.*, 1964, 130.
[8] R. Keat and R. A. Shaw, unpublished results.
[9] M. Becke-Goehring and K. John, *Angew. Chem.*, 1958, **70**, 657; M. Becke-Goehring, K. John, and E. Fluck, *Z. anorg. Chem.*, 1959, **302**, 103.

possibilities of optical and conformational isomerism). The two nongeminal bisdimethylamino-derivatives,[6] $N_3P_3Cl_4(NMe_2)_2$, m. p. 103° (XV), and m. p. 86° (XVI), react with an excess of t-butylamine in benzene in sealed tubes at 130° to give the hydrochlorides (X) and (XI), respectively, whereas reaction with an excess of t-butylamine in boiling benzene gives the free base (IX) and the hydrochloride (XI), respectively. M. p., depressions of mixed m. p., and differences in their infrared spectra prove the non-identity of the three hydrochlorides, (VIII), (X), and (XI). The free base derived from the nongeminal hydrochloride (XI) has not been prepared.

Spectroscopic evidence is available for the geminal configuration of the bis-t-butylamino-derivative (III). Reaction with an excess of dimethylamine in benzene in a sealed tube gives the compound $N_3P_3(NMe_2)_4(NHBu^t)_2$ (XII), whose dimethylamino-^{1}H nuclear magnetic resonance (n.m.r.) spectrum has only one resolvable environment, consistent with a geminal structure. Reaction of the *cis*-nongeminal tetrakisdimethylamino-derivative,[6] $N_3P_3Cl_2(NMe_2)_4$, m. p. 104° (XVII), with an excess of t-butylamine in benzene in a sealed tube gives the isomer (XIII) whose dimethylamino-^{1}H n.m.r. spectrum shows three environments, consistent with a *cis*-nongeminal structure. It has been shown earlier that the starting material (XVII) does not undergo detectable isomerisation under these conditions.[10]

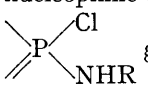
Nongeminal di- and tri-aminochlorocyclotriphosphazatrienes can undergo *cis–trans*-isomerisation in the presence of amine hydrochlorides [10] or aluminium chloride,[11] but treatment of the bis- (II) and tetrakis-t-butylamino-derivatives (III) with these reagents failed to induce any isomerisation. This by itself does not provide a conclusive argument for geminal configurations, but in conjunction with the foregoing evidence obtained by chemical and physical methods, the geminal reaction pattern shown in Scheme 1 for the replacement of chlorine by t-butylamine is regarded as established.



Scheme 1

Reaction scheme for t-butylaminochlorocyclotriphosphazatrienes

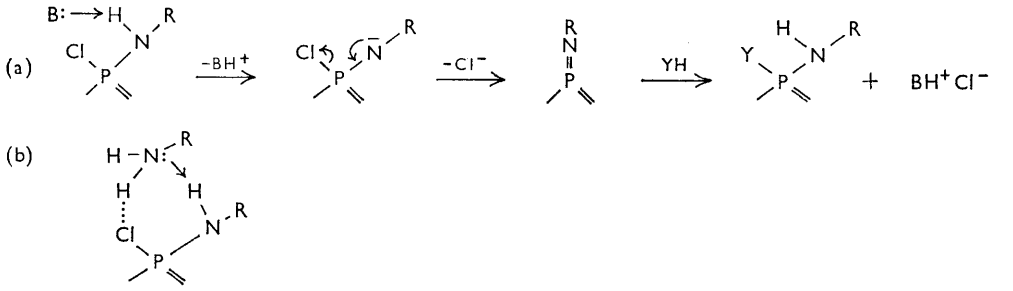
● Indicates phosphorus atom. Only t-butylamino-substituents shown. Square brackets indicate compound not observed.

Phosphazenes can be regarded as neutral ambident electrophiles. Replacement of the first chlorine atom of hexachlorocyclotriphosphazatriene by reaction with nitrogenous bases occurs by nucleophilic attack on phosphorus. Base-catalysed reactions with structures containing  groups could occur also by an alternative mechanism of proton abstraction, as shown in Scheme 2. If the proton-abstracting base, B:, contains hydrogen atoms capable of hydrogen-bonding, as in t-butylamine, this interaction might aid chloride-ion separation, possibly through a cyclic transition state as shown in Scheme 2 (*b*).

Both types of mechanism are reasonably well established for mononuclear phosphorus compounds, where kinetic evidence is available.[12] Product isolation and structure determinations throw additional light on the mechanisms in the cyclotriphosphazatriene series.

[10] R. Keat and R. A. Shaw, *Chem. and Ind.*, 1964, 1232; *J.*, 1965, 4067.
[11] R. Keat, R. A. Shaw, and C. Stratton, *J.*, 1965, 2223.
[12] F. H. Westheimer, *Chem. Soc. Special Publ.*, 1957, **8**, 181; D. Samuel and F. H. Westheimer, *Chem. and Ind.*, 1959, 51; E. W. Crunden and R. F. Hudson, *ibid.*, 1958, 1478; *J.*, 1962, 3591; R. F. Hudson in "Advances in Inorganic Chemistry and Radiochemistry," eds. H. J. Emeléus and A. G. Sharpe, Academic, New York, 1963, vol. V, p. 347.

It is significant that reactions with t-butylamine give only four different t-butylamino-derivatives, whereas nine different dimethylamino-derivatives have been obtained.[6] Replacement of the second chlorine by a t-butylamino-group occurs only in a geminal position,



Scheme 2

Proton abstraction mechanism for some aminophosphazenes

and the proton abstraction mechanism appears probable. Replacement of the fourth chlorine atom must occur at a rate comparable with, or faster than, that of the third, since no trace of a tris-t-butylamino-derivative has been detected.

Experimental

The principles of the experimental procedures are given in full in earlier Papers in this Series.[3,6] A typical reaction is described below. The light petroleum was of b. p. 60—80°. Details of the other reactions are summarised in Table 2. Analytical results are recorded in Table 3.

Table 2

Preparation of t-butylaminocyclotriphosphazatrienes

Phosphazene	(mmole)	Amine	(mmole)	Solvent	Products	Yields (%)
(I)	28	NH_2Bu^t	57	Benzene	(I)	57
					(II)	18
					(III)	8
(I)	57	NH_2Bu^t	230	Benzene	(III)	97
(I)	28	NH_2Bu^t	173	Benzene	(III)	46
					(IV)	20
(I)	28	NH_2Bu^t	173	Ether	(III)	50
					(IV)	14
(III)	10	NH_2Bu^t	20	Benzene	(III)	55
					(IV)	20
(III)	10	NH_2Bu^t	15	Benzene	(III)	75
					(IV)	5
(III)	10	NH_2Bu^t	20	Chloroform	(III)	60
					(IV)	15
(III)	10	NH_2Bu^t	15	Chloroform	(III)	81
					(IV)	3·5
(III)	10	NH_2Bu^t	20	Ether	(III)	60
					(IV)	15
(III)	10	NH_2Bu^t	15	Ether	(III)	80
					(IV)	3
(I)	28	NH_2Bu^t	340	Benzene	(IV)	96
					(V)	1·5
(IV)	5·8	NH_2Bu^t	200	Toluene *	(VI)	85
(IV)	5	$NHMe_2$	(excess)	Benzene *	(VIII)	88
(XIV)	0·05	NH_2Bu^t	(excess)	Benzene *	(VIII)	32
(XV)	11	NH_2Bu^t	(excess)	Benzene *	(IX)	72
(XV)	5	NH_2Bu^t	(excess)	Benzene *	(X)	56
(XVI)	1·45	NH_2Bu^t	(excess)	Benzene	(XI)	47
(III)	3·3	$NHMe_2$	(excess)	Benzene *	(XII)	68
(XVII)	6·5	NH_2Bu^t	(excess)	Benzene *	(XIII)	70

* Reaction carried out in sealed tube at 130°.

TABLE 3

Analyses of t-butylaminocyclotriphosphazatrienes

Compound	Found (%) C	H	Cl	N	Formula	Required (%) C	H	Cl	N
(II)	12·9	2·7	45·9	14·8	$C_4H_{10}Cl_5N_4P_3$	12·5	2·7	46·0	14·6
(III)	23·2	4·6	33·5	—	$C_8H_{20}Cl_4N_5P_3$	22·9	4·7	34·0	16·7
(IV)	39·6	8·0	14·0	—	$C_{16}H_{40}Cl_2N_7P_3$	39·0	8·0	14·3	19·8
(V)	35·8	8·0	19·7	—	$C_{16}H_{41}Cl_3N_7P_3$	36·2	7·7	20·0	18·5
(VI)	50·8	10·4	—	22·0	$C_{24}H_{60}N_9P_3$	50·8	10·5	0·0	22·2
(VII)	46·6	10·1	—	23·8	$C_{20}H_{52}N_9P_3$	46·9	10·2	0·0	24·7
(VIII)	43·8	9·7	6·3	24·0	$C_{20}H_{53}ClN_9P_3$	43·8	9·7	6·5	23·0
(IX)	46·5	10·1	—	24·9	$C_{20}H_{52}N_9P_3$	46·9	10·2	0·0	24·7
(X)	43·9	9·1	6·1	22·6	$C_{20}H_{53}ClN_9P_3$	43·8	9·7	6·5	23·0
(XI)	43·5	9·4	6·1	—	$C_{20}H_{53}ClN_9P_3$	43·8	9·7	6·5	23·0
(XII)	42·2	9·6	—	27·9	$C_{16}H_{44}N_9P_3$	42·2	9·9	0·0	27·7
(XIII)	41·7	9·5	—	28·0	$C_{16}H_{44}N_9P_3$	42·2	9·9	0·0	27·7

Reaction of Hexachlorocyclotriphosphazatriene with t-Butylamine (4 *moles*) *in Boiling Chloroform.*—t-Butylamine (17·0 g., 0·23 mole) in chloroform (25 ml.) was added slowly to a cold (−78°) stirred solution of hexachlorocyclotriphosphazatriene (I) (20·0 g., 0·057 mole) in chloroform (250 ml.). The reaction mixture was warmed to room temperature, boiled under reflux (3·5 hr.), and evaporated to dryness under reduced pressure. The crude reaction product was obtained as a colourless oil (22 g.) by extraction with light petroleum, and thin-layer-chromatographic examination showed the presence of three new components. A portion of the crude product (5·0 g.), eluted through a column containing silica gel (100 g.), gave four fractions: (*a*) eluent light petroleum (350 ml.) gave hexachlorocyclotriphosphazatriene (I) (0·65 g., 13%), m. p. and mixed m. p. 114°; (*b*) eluent light petroleum (600 ml.) and distillation of the product gave *t-butylaminopentachlorocyclotriphosphazatriene* (II) (0·6 g., 13%), b. p. 91°/0·01 mm., m. p. −10 to −11°; (*c*) eluent light petroleum–benzene (3 : 1) (2 l.) gave 6,6-*bis-t-butylamino*-2,2,4,4-*tetrachlorocyclotriphosphazatriene* (III) (1·8 g., 30%), m. p. 120—122°, on recrystallisation from light petroleum; (*d*) eluent benzene (750 ml.) gave tetrakis-t-butylaminodichlorocyclotriphosphazatriene (IV) (0·25 g., 3·5%), m. p. and mixed m. p. 156°, on recrystallisation from light petroleum.

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