396. *Phosphorus–Nitrogen Compounds. Part X.*[1] *The Aluminium Chloride-catalysed* cis–trans-*Isomerisation of Non-geminal Chlorodimethylamino- and Chloropiperidino-cyclotriphosphazatrienes*

By R. Keat, R. A. Shaw, and C. Stratton

The non-geminal bis- and tris-dimethylamino- and -piperidino-derivatives of hexachlorocyclotriphosphazatriene can be converted, by means of aluminium chloride in an inert solvent, into a mixture of *cis*- and *trans*-isomers. The non-geminal tetrakis- and the geminal bis- and tris-derivatives of these two amines do not react under these conditions. The mechanism of the reaction is discussed.

In Part V[2] of this Series, the Friedel–Crafts arylation of hexachlorocyclotriphosphazatriene, $N_3P_3Cl_6$, was described. The possibility that the quasi-phosphonium ion, $N_3P_3Cl_5^+$, or a related species, is an intermediate, and is responsible for the electrophilic substitution of the aromatic hydrocarbon was discussed.

Support for this type of ionisation comes from the work of Eley and Willis,[3] who have shown that pure solid hexachlorocyclotriphosphazatriene exhibits, under the influence of a potential difference of 12 v., a small conductivity, suggested to be due to the ionisation $N_3P_3Cl_6 \longrightarrow N_3P_3Cl_5^+ + Cl^-$.

Bode and Bach [4] claimed the isolation of an addition compound between hexachlorocyclotriphosphazatriene and aluminium chloride, formulated as $[N_3P_3Cl_4]^{2+}\ 2[AlCl_4]^-$. This doubly ionised phosphazene moiety seems a rather improbable structure,[2] but some

[1] Part IX, R. Keat and R. A. Shaw, preceding Paper.
[2] K. G. Acock, R. A. Shaw, and F. B. G. Wells, *J.*, 1964, 121.
[3] D. D. Eley and M. R. Willis, *J.*, 1963, 1534.
[4] H. Bode and H. Bach, *Chem. Ber.*, 1942, **75**, 215.

degree of ionisation of a phosphorus–chlorine bond under the influence of aluminium chloride seems likely. Phosphorus pentachloride gives a complex of composition $PCl_5.AlCl_3$, which, on the basis of ion-conductance experiments, was suggested to contain the ionic species $[PCl_4]^+ [AlCl_4^-]$.[5] Phosphorus oxychloride, $POCl_3$, also forms adducts with aluminium chloride, but here the situation is more complex because of the possibility of bond-formation by donation of electrons from the phosphoryl oxygen atom, and/or chloride ion transfer to aluminium.[6] A number of complexes have been investigated in methylene chloride solution, and, on the basis of their phosphorus-31 nuclear magnetic resonance spectra, have been assigned ionic structures of the type $[RPCl_3]^+ [AlCl_4]^-$, $[RP(O)Cl]^+ [AlCl_4]^-$, and $[RP(O)OR']^+ [AlCl_4]^-$.[7] As in the case of the organic acid halides, the bulk properties of a complex need not necessarily give an indication as to the nature of the catalytically active species. As, however, both chemical and physical evidence suggest that aluminium chloride is able to promote ionisation of phosphorus–chlorine bonds, it seemed of interest to determine whether inversion of configuration of non-geminal aminochlorocyclophosphazenes could occur under suitable conditions. Since we have recently characterised [1] the geometrical isomers of the bis-, $N_3P_3Cl_4(NMe_2)_2$, and tris-dimethylaminocyclotriphosphazatrienes, $N_3P_3Cl_3(NMe_2)_3$, and have shown that these are readily detected by means of thin-layer chromatography, they seemed suitable as a starting point for our investigation.

When 2,2,4-*trans*-6-tetrachloro-4.6-bisdimethylaminocyclotriphosphazatriene (m. p. 103°) (I) is heated at 100° in 1,1,2 2-tetrachloroethane with aluminium chloride (1 : 2 molar ratio) for 5 hours, inversion of configuration takes place, and a mixture of starting material and 2,2,4-*cis*-6-tetrachloro-4,6-bisdimethylaminocyclotriphosphazatriene (m. p. 86°) (II) is obtained. Thin-layer chromatography on silica gel enables the proportions of each isomer to be estimated.[1] The isomers were also separated by means of column chromatography on silica gel, when the m. p.s and infrared spectra could be compared with those of authentic specimens obtained from the aminolysis of hexachlorocyclotriphosphazatriene.[1] The same mixture of non-geminal bis-isomers is also obtained if the *cis*-isomer (II) is the starting material, indicating the reversibility of the isomerisation reaction. In both cases, the starting material predominated somewhat in the reaction mixture, indicating that equilibrium had not been attained.

A similar mixture of geometrical isomers is obtained on treatment of 2-*trans*-4,6-trichloro-2,4,6-trisdimethylaminocyclotriphosphazatriene (m. p. 105°) (III) with aluminium chloride under the same conditions. Here, the *trans*-isomer was still the predominant product, but 2-*cis*-4-*cis*-6-trichloro-2,4,6-trisdimethylaminocyclotriphosphazatriene (m. p. 152°) (IV) can be readily separated by means of column chromatography on silica gel or preparative-scale thin-layer chromatography on the same adsorbent.[1] Again, the reversibility of the reaction could be shown by using the *cis*-isomer (IV) as starting material, when a mixture of *cis*- and *trans*-isomers was obtained, but again complete equilibrium did not seem to have been attained.

When 2-*cis*-4-dichloro-2,4,6,6-tetrakisdimethylaminocyclotriphosphazatriene (m. p. 104°) (V) was treated similarly, no isomerisation could be detected by means of thin-layer chromatography, and the starting material was recovered in good yield. This observation parallels that in our work [1] on the dimethylaminolysis of hexachlorocyclotriphosphazatriene, where only one (the *cis*) tetrakis-derivative (m. p. 104°) (V) could be detected. It thus appears that this structure is much the preferred configuration.

Piperidino-derivatives of hexachlorocyclotriphosphazatriene, also obtained in aminolysis experiments,[8,9] have been found to undergo an analogous series of inversions in the

[5] Ya. A. Fialkov and Ya. B. Bur'yanov, *Doklady Akad. Nauk S.S.S.R.*, 1953, **92**, 585.
[6] M. Baaz, V. Gutmann, L. Hübner, F. Mairinger, and T. S. West, *Z. anorg. Chem.*, 1961, **311**, 302.
[7] F. W. Hoffmann, T. C. Simmons and L. J. Glunz *J. Amer. Chem. Soc.*, 1957, **79**, 3570.
[8] R. Keat and R. A. Shaw, unpublished results.
[9] A. A. Kropacheva, L. E. Mukhina, N. M. Kashnikova, and V. A. Parshina, *Zhur. obshchei Khim.*, 1961, **31**, 1036.

presence of aluminium chloride. Thus, the following reversible reactions are obtained under conditions similar to those in the dimethylamino-series:

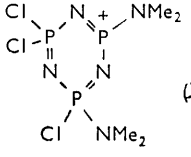
$$N_3P_3Cl_4(NC_5H_{10})_2 \text{ (m. p. 105°) (VIII)} \overset{AlCl_3}{\rightleftharpoons} N_3P_3Cl_4(NC_5H_{10})_2 \text{ (m. p. 129°) (IX)}$$

$$N_3P_3Cl_3(NC_5H_{10})_3 \text{ (m. p. 114°) (X)} \overset{AlCl_3}{\rightleftharpoons} N_3P_3Cl_3(NC_5H_{10})_3 \text{ (m. p. 190°) (XI)}$$

Again, no isomers of 2,4-dichloro-2,4,6,6-tetrakispiperidinocyclotriphosphazatriene (m. p. 111—112°) (XIII) could be obtained, paralleling our aminolysis work.[8]

Treatment of the bisdimethylamino-derivative of m. p. 62° (VI), and the trisdimethylamino-derivative of m. p. 71° (VII), with aluminium chloride under the same conditions yielded only the starting materials. This type of inversion, or attempted inversion, reaction thus provides additional evidence as to the geminal or non-geminal nature of aminochlorophosphazenes, and confirms that the bisdimethylamino-derivative of m. p. 62° (VI),[1] and the trisdimethylamino-derivative of m. p. 71° (VII) [1] are geminal, in agreement with proton nuclear magnetic resonance data.[8] A similar result was obtained for the geminal trispiperidino-derivative of m. p. −17° (XII).[8] The Table shows the results of experiments carried out on different compounds under a variety of reaction conditions.

During the working-up procedure of all the reaction mixtures, the aluminium chloride was hydrolysed by an ice-cold aqueous solution of ammonium carbonate. Thus, the possibility that inversion might have been caused by hydrogen chloride during the hydrolysis stage was reduced or eliminated. Experiments at room temperature showed that a somewhat elevated temperature was necessary for inversion to proceed at a reasonable speed.


(XIV)

In the case of the dimethylaminochlorophosphazenes, the quasi-phosphonium ion (XIV) (probably an oversimplification, cf. ref. 6) would be stabilised not only by electron delocalisation from the dimethylamino nitrogen atom, but also by delocalisation from the phosphazene ring nitrogen atoms, and hence this will facilitate phosphorus–chlorine

Aluminium chloride-catalysed inversions of aminochlorocyclotriphosphazatrienes

Compound	M. p.	Solvent	Temp.	Time (hr.)	Eluant	Products
$N_3P_3Cl_4(NMe_2)_2$ (I)	103°	$C_2H_2Cl_4$	100°	4	C_6H_6	(I) : (II) = 3 : 2
$N_3P_3Cl_4(NMe_2)_2$ (II)	86	$C_2H_2Cl_4$	100	3	C_6H_6	(I) : (II) = 1 : 2
$N_3P_3Cl_4(NMe_2)_2$ (I)	103	$C_2H_2Cl_4$	20	60	C_6H_6	(I) : (II) = 3 : 2
$N_3P_3Cl_4(NMe_2)_2$ (II)	86	$C_2H_2Cl_4$	20	60	C_6H_6	(I) : (II) = 2 : 3
$N_3P_3Cl_4(NMe_2)_2$ (I)	103	$C_2H_2Cl_4$	20	1/12	C_6H_6	(I) : (II) = 5 : 1
$N_3P_3Cl_3(NMe_2)_3$ (III)	105	$C_2H_2Cl_4$	100	3	C_6H_6	(III) : (IV) = 2 : 1
$N_3P_3Cl_3(NMe_2)_3$ (IV)	152	$C_2H_2Cl_4$	100	3	C_6H_6	(III) : (IV) = 1 : 2
$N_3P_3Cl_3(NMe_2)_3$ (III)	105	$C_2H_2Cl_4$	20	60	C_6H_6	(III) : (IV) = 5 : <1
$N_3P_3Cl_3(NMe_2)_3$ (IV)	152	$C_2H_2Cl_4$	20	60	C_6H_6	No reactn.
$N_3P_3Cl_3(NMe_2)_3$ (III)	105	$C_2H_2Cl_4$	20	1/12	C_6H_6	(III) : (IV) = 5 : <1
$N_3P_3Cl_3(NMe_2)_3$ (III)	105	$CHCl_3$	62	10	C_6H_6	(III) : (IV) = 3 : 2
$N_3P_3Cl_3(NMe_2)_3$ (III)	105	CCl_4	76	10	C_6H_6	No reactn.
$N_3P_3Cl_3(NMe_2)_3$ (III)	105	CH_3CN	82	10	C_6H_6	No reactn.
$N_3P_3Cl_2(NMe_2)_4$ (V)	104	$C_2H_2Cl_4$	100	8	C_6H_6–Et_2O *	No reactn.
$N_3P_3Cl_4(NMe_2)_2$ (VI)	62	$C_2H_2Cl_4$	100	8	C_6H_6	No reactn.
$N_3P_3Cl_3(NMe_2)_3$ (VII)	71	$C_2H_2Cl_4$	100	8	C_6H_6	No reactn.
$N_3P_3Cl_4(NC_5H_{10})_2$ (VIII)	105	$C_2H_2Cl_4$	100	6	C_6H_6–Pet. †	(VIII) : (IX) = 4 : 3
$N_3P_3Cl_4(NC_5H_{10})_2$ (IX)	129	$C_2H_2Cl_4$	100	8	C_6H_6–Pet.	(VIII) : (IX) = 3 : 2
$N_3P_3Cl_4(NC_5H_{10})_2$ (VIII)	105	$C_2H_2Cl_4$	20	60	C_6H_6–Pet.	(VIII) : (IX) = 5 : ≪1
$N_3P_3Cl_4(NC_5H_{10})_2$ (VIII)	105	$C_2H_2Cl_4$	20	1/12	C_6H_6–Pet.	No reactn.
$N_3P_3Cl_3(NC_5H_{10})_3$ (X)	114	$C_2H_2Cl_4$	20	1/12	C_6H_6–Pet.	(X) : (XI) = 5 : <1
$N_3P_3Cl_3(NC_5H_{10})_3$ (X)	114	$C_2H_2Cl_4$	100	6	C_6H_6–Pet.	(X) : (XI) = 3 : 2
$N_3P_3Cl_3(NC_5H_{10})_3$ (XI)	190	$C_2H_2Cl_4$	100	8	C_6H_6–Pet.	(X) : (XI) = 2 : 1
$N_3P_3Cl_3(NC_5H_{10})_3$ (X)	114	$C_2H_2Cl_4$	20	60	C_6H_6–Pet.	(X) : (XI) = 3 : 1
$N_3P_3Cl_3(NC_5H_{10})_3$ (X)	114	$CHCl_3$	62	10	C_6H_6–Pet.	(X) : (XI) = 3 : 2
$N_3P_3Cl_3(NC_5H_{10})_3$ (X)	114	CCl_4	76	10	C_6H_6–Pet.	No reactn.
$N_3P_3Cl_3(NC_5H_{10})_3$ (X)	114	CH_3CN	82	10	C_6H_6–Pet.	No reactn.
$N_3P_3Cl_3(NC_5H_{10})_3$ (XII)	−17	$C_2H_2Cl_4$	100	6	C_6H_6–Pet.	No reactn.
$N_3P_3Cl_2(NC_5H_{10})_4$ (XIII)	114	$C_2H_2Cl_4$	100	10	C_6H_6–Et_2O *	No reactn.

* Benzene–diethyl ether (4 : 1). † Benzene–light petroleum (b. p. 60—80°) (1 : 1).

heterolysis compared with that in the hexachloro-compound, $N_3P_3Cl_6$. The importance of this stabilisation is demonstrated by the fact that 2,2,4-*trans*-6-tetrachloro-4,6-bisdimethylaminocyclotriphosphazatriene (m. p. 103°) (I) is much more readily phenylated under Friedel–Crafts conditions than is hexachlorocyclotriphosphazatriene.[10,11] The phenylation occurs at the two phosphorus atoms carrying the dimethylamino-groups.

Varying contributions from two mechanisms can be visualised to account for the inversion. Electrophilic attack of aluminium chloride on the chlorine atom of a phosphorus–chlorine bond will result in heterolysis of this bond to give a quasi-phosphonium ion, whose lifetime will determine whether inversion will occur, *i.e.*, if the quasi-phosphonium ion has a sufficiently long life, it will have an equal probability of inversion or retention of configuration. It is possible, however, that the chloride-ion separation is also assisted by an S_N2-type nucleophilic-substitution component involving an aluminium chloride species. Rearside attack by chloride ion will probably result in inversion of configuration. Chloride-ion exchange reactions, in acetonitrile, with chlorocyclophosphazenes have been reported.[12] Both mechanistic models would predict equilibria determined by steric and electronic factors, but, in the absence of kinetic data, we are unable to distinguish between them.

In the light of the inversions reported here, as well as of those catalysed by amine hydrochlorides,[13] it should be noted that care must be taken in making structural assignments if these are based solely on the structure of a precursor or a derivative,[10] unless there is evidence to show that changes of configuration are not important in the reactions considered.

Experimental

1,1,2,2-Tetrachloroethane, chloroform, and carbon tetrachloride were distilled from phosphorus pentoxide before use. Other organic solvents were dried by using "Hi-drite" drying agent.

Previous Papers have described the preparation of the dimethylamino-derivatives,[1,14] of hexachlorocyclotriphosphazatriene used in this study. Similar methods were used to obtain piperidino-derivatives,[8,9] some of whose m. p.s (IX, XI, XII) have been reported elsewhere.[13] The preparation of the new piperidino-derivatives by the aminolysis of hexachlorocyclotriphosphazatriene will be described in a subsequent Paper.

Silica gel for thin-layer chromatography (from Merck) contained 10% calcium sulphate as a binder. Silica-gel layers were about 270 μ thick, and were activated for 1 hr. at 110° before use; eluants were as stated in the Table. Preparative-scale thin-layer chromatography was carried out on silica-gel plates (20 × 20 cm.), as previously described.[1] Thin-layer chromatograms were developed by using a chromic acid spray. Anhydrous aluminium chloride was obtained from Messrs. Hopkins and Williams.

M. p.s were determined on the hot stage of a Reichert–Kofler polarising microscope.

The inversion of 2-trans-4,6-*trichloro*-2,4,6-*trisdimethylaminocyclotriphosphazatriene* (III).—Aluminium chloride (0·71 g., 0·00532 mole) and 2-*trans*-4,6-trichloro-2,4,6-trisdimethylaminocyclotriphosphazatriene (III) (1 g., 0·00268 mole), m. p. 105°, were heated at 100° in 1,1,2,2-tetrachloroethane (10 ml.) for 6 hr. The mixture was allowed to cool, and the aluminium chloride was hydrolysed with an ice-cold aqueous 2N-ammonium carbonate solution (25 ml.). Benzene (20 ml.) was added, the mixture shaken for some minutes, and the organic layer separated. The aqueous layer was washed three times with benzene, and the washings were combined with the initially separated organic layer. This benzene solution was dried (Na_2SO_4), evaporated to small bulk, and a small portion of this was spotted onto a thin-layer plate. The plate was eluted with benzene, and development showed two spots in the approximate ratio 2 : 1. Preparative-scale thin-layer chromatography enabled the first spot to be identified as 2-*trans*-4,6-trichloro-2,4,6-trisdimethylaminocyclotriphosphazatriene, m. p. and mixed m. p. 105°, (III), and the second spot as 2-*cis*-4-*cis*-6-trichloro-2,4,6-trisdimethylaminocyclotriphosphazatriene,

[10] C. T. Ford, F. E. Dickson, and I. I. Bezman, *Inorg. Chem.*, 1964, **3**, 177.
[11] R. A. Shaw and C. Stratton, unpublished results.
[12] N. L. Paddock (quoting the results of D. B. Sowerby), *Quart. Rev.*, 1964, **18**, 168.
[13] R. Keat and R. A. Shaw, *Chem. and Ind.*, 1964, 1232.
[14] S. K. Ray and R. A. Shaw, *J.*, 1961, 872.

m. p. and mixed m. p. 152°, (IV). The infrared spectra of these isomers were identical with those obtained from authentic specimens.

Other amine derivatives were similarly treated with aluminium chloride in a ratio of 1 mole of aminochlorophosphazene to 2 moles of aluminium chloride, and the products isolated and identified. The results of these experiments are summarised in the Table.

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