751. *Phosphorus–Nitrogen Compounds. Part XII.*[1] *The* cis–trans-*Isomerisation of Non-geminal Aminochlorocyclotriphosphazatrienes by Substituted Ammonium Chlorides*

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The *cis–trans*-isomerisation of some aminochlorocyclotriphosphazatrienes, $N_3P_3Cl_{6-n}R_n$ (n = 2, 3, or 4; and R = NMe_2 or piperidino), in the presence of various substituted ammonium chlorides and in a variety of solvents has been investigated. The mechanism and consequences of these isomerisations are discussed.

IN Part X [2] of this Series, the *cis–trans*-isomerisation of nongeminal aminochlorocyclotriphosphazatrienes catalysed by aluminium chloride was reported and discussed. Similar isomerisations occur in the presence of amine hydrochlorides.[3] The positional and geometrical isomers of bis-, $N_3P_3Cl_4(NMe_2)_2$, and tris-dimethylamino-derivatives,* $N_3P_3Cl_3(NMe_2)_3$, of hexachlorocyclotriphosphazatriene, $N_3P_3Cl_6$, have recently been isolated and their structures determined by means of proton magnetic resonance spectroscopy [4–6] and dipole-moment measurements.[7] Evidence for the structural assignments of the piperidino-derivatives, used in this study will be presented elsewhere.[5] Using the knowledge thus available of the structures of these compounds, we have investigated the effects of variations of solvent, temperature, and inverting reagent on these isomerisation reactions in an attempt to show their scope, and to shed some light on their mechanism.

Table 1 shows the relative proportions of the isomers obtained under a variety of conditions. The proportions differed frequently for the same system, according to which isomer was used as the starting material; this indicated that equilibrium, determined by the properties of the aminophosphazene, and the ambient conditions, had not been attained. The isomerisation of the non-geminal *trans*-trisdimethylamino-derivative, $N_3P_3Cl_3(NMe_2)_3$ (IV) proved the most convenient route to the *cis*-isomer (V), which can only be obtained in very small quantities, and with great difficulty, from the dimethylaminolysis products of hexachlorocyclotriphosphazatriene, $N_3P_3Cl_6$.[4] As might be expected, geminal bis- and tris-dimethylamino-derivatives, compounds (III) and (IV), respectively, were unaffected on treatment with amine hydrochloride. Likewise, 2-*cis*-4-dichloro-2,4,6,6-tetrakisdimethylaminocyclotriphosphazatriene, $N_3P_3Cl_2(NMe_2)_4$, (VII), m. p. 104°, could not be isomerised, in agreement with results obtained for the isomerisation catalysed by aluminium chloride.

The isomerisation of piperidino-derivatives of hexachlorocyclotriphosphazatriene proceeds at a much slower rate, but is otherwise similar to that of the corresponding dimethylamino-derivatives. As yet this, and the isomerisation catalysed by aluminium chloride,[2] which is faster but gives poorer yields, are the only routes to the *cis*-trispiperidino-derivative (XI).

Attempts to isomerise geometrical dimethylamino-isomers by means of dimethylammonium chloride failed in benzene and ether, but could be effected in chloroform and acetonitrile. It seems unlikely that the different boiling points of these solvents play a major part in their failure or success in promoting isomerisation. As shown in Table 1, a

* For full systematic names see R. A. Shaw, B. W. Fitzsimmons, and B. C. Smith, *Chem. Rev.*, 1962, **62**, 247; and ref. 4.

[1] Part XI, B. Capon, K. Hills, and R. A. Shaw, *J.*, preceding Paper.
[2] R. Keat, R. A. Shaw, and C. Stratton, *J.*, 1965, 2223.
[3] R. Keat and R. A. Shaw, *Chem. and Ind.*, 1964, 1232.
[4] R. Keat and R. A. Shaw, *J.*, 1965, 2215.
[5] R. Keat and R. A. Shaw, unpublished results.
[6] C. T. Ford, F. E. Dickson, and I. I. Bezman, *Inorg. Chem.*, 1964, **3**, 177.
[7] H. Koopman, I.U.P.A.C. Conference, London, 1963, Abstracts AB-4/136, and personal communication.

variety of substituted ammonium chlorides were used in attempts to promote isomerisation. Of the methylammonium chlorides only the di- and tri-methyl derivatives were able to effect inversions in chloroform. Table 2 reveals that this ability can be at least partially related to the solubilities of these methylammonium chlorides in this solvent.

TABLE 1

The *cis–trans*-isomerisation of chlorodimethylamino- and chloropiperidinocyclotriphosphazatrienes in the presence of alkylammonium chlorides

Compound		M. p.	Structure	Inverting reagent	Solvent	Time (hr.)	Temp.	Products
$N_3P_3Cl_4(NMe_2)_2$	(I)	103°	*trans*	NH_2Me_2Cl	$CHCl_3$	8	61°	(I) : (II) = 3 : 1
,,	(II)	86	*cis*	,,	,,	,,	,,	(I) : (II) = 1 : 2
,,	(III)	62	geminal	,,	,,	,,	,,	(III) only
$N_3P_3Cl_3(NMe_2)_3$	(IV)	105	*trans*	,,	,,	,,	,,	(IV) : (V) = 2 : 1
,,	(V)	152	*cis*	,,	,,	12	,,	(IV) : (V) = 1 : 3
,,	(VI)	71	geminal	,,	,,	8	,,	(VI) only)
$N_3P_3Cl_2(NMe_2)_4$	(VII)	104	*cis*	,,	,,	12	,,	(VII) + traces (IV) and (V)
$N_3P_3Cl_3(NMe_2)_3$	(IV)	105	*trans*	NH_3Bu^tCl	,,	8	,,	(IV) only
,,	(IV)	,,	,,	NH_3MeCl	,,	36	,,	(IV) only
,,	(IV)	,,	,,	NMe_3Cl	,,	24	,,	(IV) : (V) = 3 : 1
$N_3P_3Cl_4(NMe_2)_2$	(I)	103	,,	,,	,,	,,	,,	(I) : (II) = 2 : 1
$N_3P_3Cl_3(NMe_2)_3$	(IV)	105	,,	NMe_4Cl	,,	,,	,,	(IV) only
,,		,,	,,	,,	MeCN	,,	82	(IV) : (V) = 1 : 1
,,		,,	,,	NH_3MeCl	,,	,,	,,	(IV) : (V) = 3 : 1
,,		,,	,,	$NH_2C_5H_{10}Cl$	$CHCl_3$	,,	61	(IV) : (V) = 3 : 2
$N_3P_3Cl_4(NMe_2)_2$	(I)	103	,,	,,	,,	,,	,,	(I) : (II) = 5 : 1
,,		,,	,,	NH_2Me_2Cl	,,	48	20	(I) only
$N_3P_3Cl_3(NMe_2)_3$	(IV)	105	,,	,,	,,	,,	,,	(IV) only
,,		,,	,,	NBu^n_4Cl	,,	8	61	(IV) : (V) = 3 : 2
,,		,,	,,	NBu^n_4Cl	MeCN	,,	82	(IV) : (V) = 3 : 2
,,		,,	,,	LiCl	C_5H_5N	24	115	(IV) : (V) = 5 : 1
$N_3P_3Cl_4(NC_5H_{10})_2$	(VIII)	104—105	,,	$NH_2C_5H_{10}Cl$	$CHCl_3$	12	61	(VIII) only
,,	(IX)	129	*cis*	,,	,,	,,	,,	(IX) only
$N_3P_3Cl_3(NC_5H_{10})_3$	(X)	104·5	*trans*	,,	,,	60	,,	(X) : (XI = 3 : 2
,,	(XI)	190	*cis*	,,	,,	20	,,	(X) : (XI) = 1 : 3
,,	(XII)	−17	geminal	,,	,,	24	,,	(XII) only
$N_3P_3Cl_2(NC_5H_{10})_4$	(XIII)	111—112·5	*cis*	,,	,,	48	,,	(XIII) only
$N_3P_3Cl_4(NC_5H_{10})_2$	(VIII)	104—105	*trans*	,,	MeCN	12	82	(VIII) only
,,		,,	,,	NH_2Me_2Cl	$CHCl_3$	,,	61	(VIII) : (IX) = 5 : <1

Numerous attempts to isomerise the above compounds with alkylammonium chlorides in ether and benzene were unsuccessful.

TABLE 2

The solubilities of alkylammonium chlorides in various solvents

Compound	Solvent	Dielectric const. at 20°	Solubility (g./100 ml. of solvent at b. p.)
NH_3MeCl	$CHCl_3$	5·1	0·004
NH_2Me_2Cl	,,	,,	28·8
$NHMe_3Cl$	,,	,,	16·0
NMe_4Cl	,,	,,	0·2
$NH_2C_5H_{10}Cl$	,,	,,	12·5
NH_3MeCl	MeCN	38·8	0·1
NMe_4Cl	,,	,,	0·5
NH_2Me_2Cl	PhH	2·2	0·4
NH_2Me_2Cl	Et_2O	4·3	0·2

It is probably for the same reason that tetra-n-butylammonium chloride is an effective inverting reagent, in contrast to tetramethylammonium chloride, the former being highly, the latter only sparingly, soluble in this solvent. This cannot, however, be the only significant factor as the non-geminal bispiperidides, $N_3P_3Cl_4(NC_5H_{10})_2$, (VIII) and (IX),

do not invert with piperidinium chloride in chloroform or acetonitrile, whilst isomerisation is achieved, albeit slowly, by means of dimethylammonium chloride in chloroform, and yet both amine hydrochlorides possess solubilities of the same order in this solvent.

It is also notable that the trispiperidino-derivatives, (X) and (XI), undergo inversion more readily than the corresponding bispiperidino-derivatives, (VIII) and (IX); it may well be that the greater electron supply in the tris-derivatives favours a mechanism in which bond-breaking is more important than in the bispiperidides. Tetramethylammonium chloride in chloroform, dimethylammonium chloride in benzene or ether, and methyl- and tetramethyl-ammonium chloride in acetonitrile all exhibit similar solubilities, but only the last two systems were found to be effective for inversions, which suggests that the dielectric constant of the medium is of considerable significance.

The list of chlorides employed in isomerisation studies is by no means confined to methylammonium and piperidinium chlorides; for example pyridinium chloride,[8] tetra-n-butylammonium chloride, and lithium chloride are able to promote inversions, as are probably many other halide salts. As shown in Table 1, dimethylamino- and piperidino-derivatives can be inverted by a variety of alkylammonium chlorides without any foreign amino-groups being found in the resultant mixture of *cis*- and *trans*-isomers. This indicates that exocyclic phosphorus–nitrogen bonds are neither broken nor formed in the isomerisation process. Further evidence for such a chloride-ion exchange comes from the work of Sowerby,[9] who observed that radioactive chloride ions derived from tetraethylammonium chloride exchange quite rapidly with hexachlorocyclotriphosphazatriene in acetonitrile at 25°. Similarly, exchange may well take place also at the $\equiv PCl_2$ groupings of the compounds we have investigated, but would of course not have been detected by our methods.

The above inversion reactions may arise either through a bimolecular displacement at the phosphorus atom, which in some cases may lead to five-co-ordinate intermediates (cf. ref. 1), or through a unimolecular ionisation of the phosphorus–chlorine bond followed by rapid phosphazenylation. Inversion of configuration could equally well occur with either mechanism. The observed rapid racemisation of optically active phosphorochloridates by chloride ions [10] is most pertinent to our inversion reactions. In general, in homogeneous solution, most replacement reactions at phosphorus in mononuclear phosphorus compounds are accompanied by inversion of configuration.[11] This can be seen to hold true also for the isomerisations of the phosphazenes reported here, in so far as they are effected by a bimolecular reaction.

Since amine hydrochlorides are products of the aminolysis reactions of chlorophosphazenes, care must be exercised in drawing conclusions about the structure of a compound from a knowledge of the stereochemistry of its precursor. Although the solvent used for aminolysis may not be as good a solvent for amine hydrochlorides as chloroform, the addition of excess of amine can bring about conditions favourable for isomerisation. Recent observations,[4,5] based on the reactions of dimethylamino- and piperidino-derivatives, indicate that isomerisations by amine hydrochlorides during aminolysis by aliphatic amines do not play a major role; in these systems apparently, the rates of aminolysis compare favourably with those of inversion. This observation is, however, not of universal validity, and with less effective nucleophiles, inversion reactions may and do compete with replacement reactions.[8]

Experimental

The preparation of dimethylamino-derivatives of hexachlorocyclotriphosphazatriene has been described in detail,[4] and routes to piperidino-derivatives will be reported elsewhere.[5] Amine hydrochlorides (Hopkins and Williams) were dried *in vacuo* at 60° for 1 hr. before use.

[8] D. Dell, B. W. Fitzsimmons, and R. A. Shaw, unpublished results.
[9] D. B. Sowerby, quoted by C. D. Schmulbach, *Prog. Inorg. Chem.*, 1962, **4**, 366; and by N. L. Paddock, *Quart. Rev.*, 1964, **18**, 168.
[10] H. S. Aaron, R. T. Uyeda, H. F. Frack, and J. I. Miller, *J. Amer. Chem. Soc.*, 1962, **84**, 617.
[11] R. F. Hudson, *Adv. Inorg. Chem. Radiochem.*, 1964, **5**, 347.

Light petroleum, benzene, and ether were dried by standing them over "Hidrite" drying agent. Chloroform and acetonitrile were dried by distillation from phosphoric oxide.

Melting points were determined on a Reichert–Kofler micro-heating stage fitted with a polarising microscope.

Thin-layer chromatograms were run on silica gel containing 10% calcium sulphate from Merck Ltd. Layers were activated for 1 hr. at 110°. The approximate relative proportions of each isomer were determined by comparison of the size and intensity of the spots produced on development of the thin-layer chromatograms. The eluant for bis- and tris-dimethylamino-derivatives was benzene, for the corresponding piperidino-derivatives benzene–light petroleum (b. p. 60—80°) (1 : 1). Both tetrakis-derivatives were eluted with benzene–ether (4 : 1). The solubilities of the alkylammonium chlorides in various solvents were measured by removal of a known volume of solution boiling under reflux with an excess of chloride. The solvent was evaporated from the removed solution and the residue weighed.

Isomerisations.—Only one isomerisation is described in detail, the remainder, being similar, are summarised in Table 1.

Isomerisation of 2-trans-4,6-*trichloro*-2,4,6-*trispiperidinocyclotriphosphazatriene* (X). The *trans*-trispiperidino-derivative (X) (0·5 g., 0·00101 mole) and piperidinium chloride (0·61 g., 0·00505 mole) were dissolved in chloroform (20 ml.). The mixture was boiled under reflux in an atmosphere of dry nitrogen for 60 hr. The chloroform was removed under reduced pressure and the residue extracted with hot light petroleum (b. p. 60—80°) (50 ml.). The piperidinium chloride was filtered off and the volume of the filtrate reduced to about 3 ml. Analytical-scale thin-layer chromatography showed that two compounds were present in an approximately 3 : 2 ratio. These were separated by preparative-scale thin-layer chromatography as described in an earlier Paper.[4] The identity of the isomers was checked by m. p. and mixed m. p. with authentic specimens, and further confirmed by comparison of their infrared spectra. The isomers thus obtained were the starting material, (X), m. p. 114·5° and 2-cis-4-cis-6-*trichloro*-2,4,6-*trispiperidinocyclotriphosphazatriene*, (XI) m. p. 190° (Found: C, 36·8; H, 5·95; Cl, 21·8. $C_{15}H_{30}Cl_3N_6P_3$ requires C, 36·5; H, 6·1; Cl, 21·6%).

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