Preparation and Nuclear Magnetic Resonance Spectra of the Chloromonofluorocyclophosphazenes

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The cyclic chlorophosphazenes $N_nP_nCl_{2n}$ (n = 3—6) are fluorinated by a mixture of SbF_3 and $SbCl_5$ to give either the monofluoro-compound or, depending on the reagent ratio, mixtures of non-geminal chloride fluorides. The n.m.r. parameters of the monofluorides show similar ring-size effects to the monochlorofluorocyclophosphazenes.

Two principal methods have been used for the preparation of chlorofluorocyclophosphazenes from the cyclic chlorides $N_nP_nCl_{2n}$. The use of anionic reagents such as sodium fluoride or potassium fluorosulphite has the longer history. These reagents react easily with the trimeric,[1] tetrameric,[1] and pentameric [2] chlorides, but the reaction is not very suitable for the preparation of the individual compounds because fluorine substitution accelerates the reaction and a spectrum of derivatives is obtained. The second method uses antimony trifluoride.[3] It is inherently more suitable for the directed synthesis of chlorofluorophosphazenes because its action depends on its preliminary co-ordination to a ring nitrogen atom.[3] Progressive fluorination would weaken the donor properties of the phosphazene and so limit the extent of fluorination. By itself, SbF_3 is too weak an acceptor to react with $N_3P_3Cl_6$.[4] Reaction occurs when the base strength of the phosphazene is increased by dimethylamination, and fluorination of the bis-,[3] tris-,[4] and tetrakis-(dimethylamino)-chlorocyclophosphazenes [4] by SbF_3 usually takes place non-geminally. Treatment of the products with hydrogen chloride then gives the chloride fluorides.[5] By using the two methods, all compounds in the $N_3P_3Cl_{6-x}F_x$ series, both geminal and non-geminal, have now been made.

Neither method is entirely suitable for the preparation of monosubstituted derivatives in high yield. The monochlorofluorocyclophosphazenes have been obtained by the action of HCl on the dimethylamino-derivatives $N_nP_nF_{2n-1}(NMe_2)$ (n = 3 [6,7] or 4—6 [6]), but there is no general method for making the monofluorides $N_nP_nCl_{2n-1}F$. It was suggested earlier [3] that, although SbF_3 does not fluorinate the PCl_2 groups in chloro(dimethylamino)-phosphazenes, it might do so if antimony pentachloride were added. It seemed possible to us that an SbF_3–$SbCl_5$ mixture, the conventional Swarts reagent, might fluorinate the cyclic chlorides themselves, and so provide a convenient route to the monofluoro-derivatives. The idea is supported by the recent finding [8] that $SbCl_5$ promotes the fluorination of $N_3P_3Cl_5(NMe_2)$, which is too weakly basic to react with SbF_3 alone.[4] We have found that moderate yields of the monofluoro-compounds $N_nP_nCl_{2n-1}F$ are obtained by the action of an SbF_3–$SbCl_5$ mixture on the cyclic chlorides (n = 3—6). The method described below appears to be a useful extension of the two basic procedures. The monofluorides are now available in moderate yields, by using a one-step procedure; also, the use of SbF_3–$SbCl_5$ instead of $K[SFO_2]$ produces a sharper distribution of products, so that the method may be useful for the systematic investigation of the non-geminal chloride fluorides of the larger cyclic phosphazenes. The advantages are somewhat offset by the decomposition reactions, which have not been investigated.

RESULTS AND DISCUSSION

The n.m.r. spectra of the monofluorides have the expected primary structure. For all four compounds, the ^{19}F spectrum is a doublet of triplets [^1J(PF), ^3J(PF)]. The ^{31}P spectrum also shows a doublet of triplets [^1J(PF), ^2J(PP)] from the PClF group and an incompletely resolved multiplet from the PCl_2 groups. This approximate treatment has been refined by a complete analysis [9] of the spectra of $N_3P_3Cl_5F$, which are the most complicated of the series because of the nearness of the PCl_2 bands to the lower-field PClF triplet. In the larger-ring compounds the separation is increased, and the spectra are closer to first order. There is no ambiguity in choosing the major peak of the PClF triplets, and shifts and coupling constants determined directly from frequency differences are given in Table 1, where they are given primes to denote approximation. Comparison with the results of the complete analysis (Table 1) shows that ^1J(PF)′ (the least accurate parameter) is in error by 8—14 Hz. The improved approximation to first-order behaviour is expected to reduce this error for the other compounds; for $N_6P_6ClF_{11}$ the improvement is sufficient to allow the assessment of ^3J(PF) as 20 Hz. The PCl_2 part of the ^{31}P spectrum is complex, long-range coupling being significant. A first-order treatment is inapplicable, but the observed transitions are too few for an iterative analysis. Within the same molecule, the chemical shifts of the phosphorus atoms in PCl_2 groups in different environments differ by 2 p.p.m. at most, and are averaged in Table 1. The n.m.r. parameters obtained in this way have three points of interest. (*i*) The pattern of fluorine shifts of the PClF group is the same for the monofluoride and the monochloride series, $N_3P_3 <$

[1] J. Emsley and N. L. Paddock, *J. Chem. Soc.* (*A*), 1968, 2590.
[2] N. L. Paddock and J. Serreqi, *Canad. J. Chem.*, 1974, **52**, 2546.
[3] B. Green and D. B. Sowerby, *J. Chem. Soc.* (*A*), 1970, 987.
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[6] T. Chivers and N. L. Paddock, *Chem. Comm.*, 1969, 337; T. Chivers, R. T. Oakley, and N. L. Paddock, *J. Chem. Soc.* (*A*), 1970, 2324.
[7] O. Glemser, E. Niecke, and H. W. Roesky, *Chem. Comm.*, 1969, 282.
[8] B. Green, *J.C.S. Dalton*, 1974, 1113.
[9] F. Heatley and S. M. Todd, *J. Chem. Soc.*(*A*), 1966, 1152.

$N_4P_4 > N_5P_5 > N_6P_6$; in both series the shift and coupling constant vary in opposite senses. (*ii*) Remarkably, corresponding parameters are very similar for the two series, suggesting that chlorophosphazene and fluorophosphazene rings have similar electronic influences on a PClF group. (*iii*) In the $N_nP_nCl_{2n-1}F$ series, the difference between the phosphorus shifts of the PClF and PCl_2 groups decreases as the ring size is increased, suggesting that the electrical effect of the fluorine atom is transmitted effectively within the ring; a similar conclusion can be drawn from a comparison of the shifts of the PCl_2 groups in the chlorides and the monofluorochlorides (Table 1).

EXPERIMENTAL

The following general procedure was used; quantities are given in Table 2. A solution of the chlorophosphazene pentane or dichloromethane, and the mixture was separated by g.l.c.; typical column temperatures for N_3P_3 and N_6P_6 chloride fluorides were 170 and 275 °C. When the retention time of the desired product (*e.g.* $N_3P_3Cl_5F$) was close to that of $SbCl_3$, a few drops of water were added to the pentane solution to precipitate the antimony as a basic salt. The solution was dried with $Na_2[SO_4]$ and separated by g.l.c. The products (Table 2) were purified by recrystallisation from pentane at −80 °C.

Products.—All microanalyses were by Mr. P. Borda. Pentachlorofluorocyclotriphosphazene, m.p. 43—45 °C (lit.,[1] 50 °C) (Found: Cl, 53.7; N, 12.7. Calc. for Cl_5FNP_3: Cl, 53.5; N, 12.7); heptachlorofluorocyclotetraphosphazene, m.p. 59—61 °C (lit., 63 °C) (Found: Cl, 55.8; N, 12.6. Calc. for $Cl_7FN_4P_4$: Cl, 58.6; N, 12.5); hexachlorodifluorocyclotetraphosphazene, m.p. 27—29 °C (Found: Cl, 49.7; N, 12.8. Calc. for $Cl_6F_2N_4P_4$: Cl, 49.4; N, 13.0); pentachlorotrifluorocyclotetraphosphazene, m.p. 3.0—7.5 °C (Found:

TABLE 1

N.m.r. parameters [a] of $N_nP_nCl_{2n-1}F$ and $N_nP_nF_{2n-1}Cl$ [b]

Compound	δ_F'	δ_P'(PClF)	δ_P'(PCl_2) [c]	^1J(PF)′ [d]	^2J(PP)′	Compound	δ_F'(PClF)	^2J(PF)′
		p.p.m.		Hz			p.p.m.	Hz
$N_3P_3Cl_5F$ [e]	30.1	97.8	89.5	1 026 (1 020)	79	$N_3P_3ClF_5$	30.7	994
$N_4P_4Cl_7F$	39.3	123.5	118.9	970 (968)	64	$N_4P_4ClF_7$	38.2	924
$N_5P_5Cl_9F$ [f]	36.5	128.9	127.6	970 (968)	65	$N_5P_5ClF_9$	33.9	952
$N_6P_6Cl_{11}F$	34.9	128.1	127.5	996 (998)	48	$N_6P_6ClF_{11}$	32.8	974

[a] ^{19}F and ^{31}P spectra were recorded on Varian HA100 and XL100 instruments respectively. Shifts (positive, upfield) relative to internal $CFCl_3$ or external P_4O_6. Coupling constants were measured to first order. [b] Comparison data from R. T. Oakley and N. L. Paddock, *J. Chem. Soc.* (*A*), 1970, 2324. [c] For comparison, δ_P of chlorides, relative to P_4O_6 (assumed 112.5 p.p.m. downfield of H_3PO_4): $N_3P_3Cl_6$, 92.8; $N_4P_4Cl_8$, 119.8; $N_5P_5Cl_{10}$, 129.5; $N_6P_6Cl_{12}$, 128.5 p.p.m. (H. R. Allcock, 'Phosphorus–Nitrogen Compounds,' Academic Press, New York, 1972, p. 401). [d] Figures in parentheses from phosphorus spectrum. [e] Complete analysis of the phosphorus spectrum (ref. 9): δ_P(PClF) 98.1 and δ_P(PCl_2) 89.5 p.p.m. (converted from H_3PO_4 to P_4O_6 reference); ^1J(PF) 1 012, ^2J(PP) 78.5 ± 0.5 Hz. [f] Lit.,[2] δ_F' 36.4 p.p.m. and ^2J(PP)′ 968 Hz.

TABLE 2

Reaction of $(NPCl_2)_n$ with SbF_3–$SbCl_5$

	Amount of reactants (mmol)			Amount of products, $N_nP_nCl_{2n-x}F_x$ (mmol)				Yield/%	
n	$(NPCl_2)_n$	SbF_3	$SbCl_5$	$x = 0$	1	2	3	Total [a]	Monofluoride [b]
3	10.6	31.8	3.0	0.86	2.4	*c*		25	100
4	8.65	8.9	1.0	1.0	2.6	1.15		49	69
4	8.65	26.8	2.7		*c*	2.1	1.8	45	0
4 [d]	17.3	55.9	6.7	1.1	3.8	3.6	*c*	46	51
5	6.9	6.7	1.0	0.86	2.1	0.6	0.1	48	63
5	3.45	7.3	1.0		0.2	1.1	1.1 [e]	72	9
6	7.2	8.9	1.3	0.7	1.2	0.6	0.1	30	63
6	4.3	12.8	2.0			0.45	0.45 [f]	36	0

[a] Chloride fluorides, based on chloride used. [b] Monofluoride, based on total chloride fluorides. [c] Trace amount. [d] Reaction stopped before completion. [e] Also when $x = 4$, amount 0.1 mmol. [f] Also when $x = 4$, amount 0.4 mmol.

(0.2—0.4 mol dm^{-3} in 1,1,2,2-tetrachloroethane) was treated with finely divided SbF_3 which had been dried at 150 °C *in vacuo*. Antimony pentachloride (1 mol dm^{-3} in $CHCl_2CHCl_2$) was added over 5—10 min to the refluxing and vigorously stirred solution. The reaction is heterogeneous, and the reaction times were consequently incompletely reproducible over the range 40—80 min. It was useful to monitor the reaction by g.l.c. (Varian Aerograph 90-P; column, 5 ft × ⅜ in diameter; 20% silicone rubber SE30 on Chromasorb W, 60—80 mesh), either to stop the reaction at a particular point or to show the need for further small amounts of SbF_3 and $SbCl_5$. When the reaction had reached the required stage, the solution was decanted from the black residue, and the solvent evaporated off *in vacuo*, until crystals of $SbCl_3$ began to sublime. The residue was then extracted with n-pentane, and the solvent removed from the extract. The residue was re-extracted, either with

Cl, 43.0; N, 13.2. Calc. for $Cl_5F_3N_4P_4$: Cl, 42.7; N, 13.5); nonachlorofluorocyclopentaphosphazene, m.p. 10—11 °C (Found: Cl, 56.7; F, 3.1; N, 12.4. Calc. for $Cl_9FN_5P_5$: Cl, 56.7; F, 3.4; N, 12.4); octachlorodifluorocyclopentaphosphazene (Found: Cl, 51.6; N, 12.6. Calc. for $Cl_8F_2N_5P_5$: Cl, 51.8; N, 12.8); heptachlorotrifluorocyclopentaphosphazene (Found: Cl, 46.3; N, 13.0. Calc. for $Cl_7F_3N_5P_5$: C, 46.8; N, 13.2); *undecachlorofluorocyclohexaphosphazene*, m.p. 64—65 °C (Found: Cl, 57.4; F, 2.7. $Cl_{11}FN_6P_6$ requires Cl, 57.5; F, 2.8); decachlorodifluorocyclohexaphosphazene, m.p. 37—39 °C (Found: Cl, 53.4; N, 12.7. Calc. for $Cl_{10}F_2N_6P_6$: Cl, 53.5; N, 12.7); nonachlorotrifluorocyclohexaphosphazene, m.p. 12—13 °C (Found: Cl, 48.2; N, 12.7. Calc. for $Cl_9F_3N_6P_6$: Cl, 49.4; N, 13.0); octachlorotetrafluorocyclohexaphosphazene, m.p. −13.5 to −12 °C (Found: Cl, 44.8; N, 12.9. Calc. for $Cl_8F_4N_6P_6$: Cl, 45.0; N, 13.3%).

N.m.r. Spectra.—The parameters deduced from the ^{19}F and ^{31}P spectra of the monofluoro-compounds are given in Table 1. The ^{19}F spectra of the multiply fluorinated products (Table 2, $x = 2$—4) all showed a pair of peaks characteristic of the PClF group, with a chemical shift *ca.* 1 p.p.m. to low field of the monofluoro-compound of the same ring size; $J(PF)'$ 950—1 000 Hz. The complicated structure of the individual peaks and a partial g.l.c. analysis suggested that the products were mixtures of isomers. The spectra showed the substitution pattern to be exclusively non-geminal in the early stages, except that bands corresponding to PF_2 groups were present in the spectra of $N_6P_6Cl_3F_9$ [δ_F' 68 p.p.m., $^1J(PF)'$ 990 Hz, PF_2 : PClF = 1 : 30) and $N_6P_6Cl_4F_8$ [δ_F' 69 p.p.m., $^1J(PF)'$ 1 000 Hz, PF_2 : PClF = 1 : 8). Apparently, a small amount of geminal substitution can take place if the ring is large enough.

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