Cyclic Inorganic Compounds. Part XIII.[1] The Non-geminal Bromofluoro- and Chlorofluoro-cyclotriphosphazenes

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Cyclotriphosphazenes substituted non-geminally by fluorine and either chlorine or bromine have been prepared. The compounds, with general formula $P_3N_3F_nX_{6-n}$ where X = Cl or Br and n = 2—4, result from reactions under pressure between either hydrogen chloride or bromide and dimethylaminofluorocyclotriphosphazenes. The more volatile chlorofluoro-compounds can be prepared at atmospheric pressure by passing hydrogen chloride through a refluxing solution of the aminofluoride in nitrobenzene. In all cases, pairs of *cis–trans*-isomers are obtained. Structures have been assigned to the products on the basis of ^{19}F n.m.r. spectra.

REACTIONS between various anionic fluorinating agents [2] and both hexachlorocyclotriphosphazene and octachlorocyclotetraphosphazene give, in addition to completely fluorinated products, series of mixed chlorofluoro-derivatives $P_3N_3F_nCl_{6-n}$ and $P_4N_4F_nCl_{8-n}$. These products are exclusively the geminal isomers, *i.e.*, those in which chlorine atoms at the same phosphorus atom are substituted. The geminal substitution scheme also seems to be followed in fluorination of the hexabromide.[3] The non-geminally substituted mixed halides must therefore be obtained by an indirect route.

We have shown that non-geminal trimeric [4] and tetrameric [5] compounds can be obtained from the reaction of dimethylaminofluorocyclophosphazenes, in which fluorine atoms are known to occupy non-geminal positions, with either anhydrous hydrogen chloride or bromide, *e.g.*, reactions (1) and (2). Similar reactions

$$P_3N_3F_n(NMe_2)_{6-n} + 2nHX \longrightarrow P_3N_3F_nX_{6-n} + nMe_2NH\cdot HX \quad (1)$$

$$P_4N_4F_n(NMe_2)_{8-n} + 2nHX \longrightarrow P_4N_4F_nX_{8-n} + nMe_2NH\cdot HX \quad (2)$$

have been reported by Paddock [6] and Glemser [7] and their co-workers. In this paper, the preparation and identi-

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[1] Part XII, D. Millington and D. B. Sowerby, *J.C.S. Dalton*, 1972, 2035.

[2] J. Emsley and N. L. Paddock, *J. Chem. Soc.* (*A*), 1968, 2590.

[3] E. Steger and D. Klemm, *J. Inorg. Nuclear Chem.*, 1967, **29**, 1812.

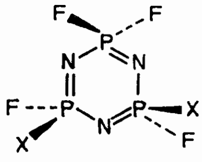
[4] B. Green and D. B. Sowerby, *Chem. Comm.*, 1969, 628.

[5] B. Green and D. B. Sowerby, *Inorg. Nuclear Chem. Letters*, 1969, **5**, 989.

[6] T. Chivers, R. T. Oakley, and N. L. Paddock, *J. Chem. Soc.* (*A*), 1970, 2324.

[7] O. Glemser, E. Niecke, and H. Thamm, *Z. Naturforsch.*, 1970, **25b**, 754.

fication of the complete series of non-geminally substituted trimeric chloride fluorides and bromide fluorides, $P_3N_3F_nX_{6-n}$ where $n = 2$—4 and X = Cl or Br [compounds (I)—(XII)], is reported; *cis–trans*-isomer pairs exist for each stoicheiometry.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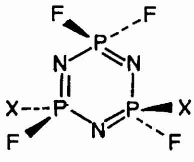
(VII ; X = Cl)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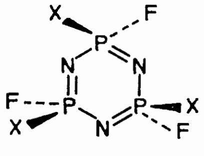
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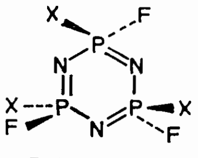
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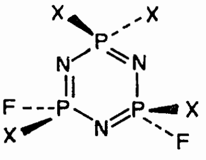
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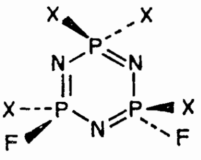
(VI ; X = Br)
(XII ; X = Cl)

EXPERIMENTAL

Dimethylaminofluorocyclotriphosphazenes were prepared as described.[8,9]

Reactions under Pressure.—Purified hydrogen chloride or bromide (20% excess) was condensed on the degassed aminofluorocyclotriphosphazene (*ca.* 5 g) in a Carius tube (25 ml volume) which was sealed under vacuum. The tube was placed in a rocking autoclave and a compensating pressure of nitrogen was applied to the bomb as the temperature was raised (see Table 1). As reaction proceeded, the pressure was reduced and after the time given in Table 1 the system was cooled. Excess of hydrogen halide was removed at 0 °C on a vacuum line and the product was distilled from room temperature to a liquid-nitrogen trap.

TABLE 1

Preparative data

			cis : *trans*-Ratio		N(%)		Reaction conditions	
Compound	Yield (%)	B.p./°C	Starting material	Product	Found	Calc.	t/°C	time/h
$P_3N_3F_4Br_2$	90	151	13·5 : 86·5	55 : 45	10·8	11·3	100	24
$P_3N_3F_3Br_3$	80	205 (76) [a]	4·5 : 95·5	24·5 : 75·5	9·4	9·7	100	36
$P_3N_3F_2Br_4$	50	253—255 [b]			8·4	8·5		
$P_3N_3F_4Cl_2$	84	114	13·5 : 86·5	50 : 50	14·7	14·9	120	90
$P_3N_3F_3Cl_3$	90	148 (44) [a]	0 : 100	20 : 80	14·2	14·1	120	120
$P_3N_3F_2Cl_4$	65	187	20 : 80		13·1	13·3	120	220

[a] M.p. of pure *cis*-isomer. [b] Darkens above 200 °C.

Some difficulty was experienced with the HBr–$P_3N_3F_2(NMe_2)_4$ reaction as short reaction times gave intermediates whilst prolonged reaction gave decomposition products only. In a series of experiments where the reactants were in contact for various times at different temperatures, the final product never contained more than 50% of $P_3N_3F_2Br_4$. The bulk of the remainder was made up of isomers with the stoicheiometry $P_3N_3F_2Br_3NMe_2$. A sample of the tetrabromide was obtained by extracting the reaction mixture with light petroleum and separating the required product from the monoamide by preparative g.l.c.

In a reaction of $P_3N_3F_2(NMe_2)_4$ where the hydrogen bromide was added in aliquot portions, after a total of 15 h at 100 °C the product was essentially $P_3N_3F_2Br_3NMe_2$. The liquid was purified by vacuum distillation (Found: C, 5·1; H, 1·3; N, 10·9. Calc. for $P_3N_3F_2Br_3NMe_2$: C, 5·3; H, 1·3; N, 11·8%).

No side reaction occurred with hydrogen chloride, but with hydrogen bromide the amine hydrobromide was invariably dark coloured. In some experiments free bromine and phosphorus tribromide were isolated showing complete decomposition of the cyclophosphazene. One of the initial decomposition products is phosphorus pentabromide which has been observed by mass spectrometry, but phosphorus bromide fluorides are also likely to be involved.

Liquids consisting of pairs of *cis–trans*-isomers were obtained in all experiments but they could not be separated by distillation. However, with $P_3N_3F_2Cl_4$ and $P_3N_3F_2Br_4$ as exceptions, preparative g.l.c. gave samples of the pure isomers. Table 1 summarizes information on the *cis–trans*-isomer ratio of the products and of the aminofluoride starting materials, the b.p.s of the isomer mixtures, and nitrogen analyses. Mass spectrometry confirmed both the stoicheiometry of the separated isomers and the absence of contaminants.

Reactions at Atmospheric Pressure.—In a typical reaction a stream of hydrogen chloride was passed for 13 h through a solution of *trans*-$P_3N_3F_3(NMe_2)_3$ in nitrobenzene. The temperature was held at 150 °C and the product $P_3N_3F_3Cl_3$ was removed from the gas stream by passage through a trap at −78 °C. Moisture was kept from the system by a non-return valve filled with liquid paraffin. The product in the trap, contaminated by small quantities of nitrobenzene, was purified by preparative g.l.c., giving a 73% yield of the mixed *cis–trans*-isomers. A similar high yield of $P_3N_3F_4Cl_2$ was obtained from $P_3N_3F_4(NMe_2)_2$ but with the less volatile

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[8] B. Green and D. B. Sowerby, *J. Chem. Soc.* (*A*), 1970, 987.

[9] B. Green, D. B. Sowerby, and P. Clare, *J. Chem. Soc.* (*A*), 1971, 3487.

$P_3N_3F_2Cl_4$ isomers the yield from $P_3N_3F_2Cl_2(NMe_2)_2$ (1,3-difluoride) starting material dropped to 22%. An intermediate, $P_3N_3F_4Cl(NMe_2)$, made up *ca.* 7% of the product from the $P_3N_3F_4(NMe_2)_2$ reaction, and after separation by preparative g.l.c. it was identified by mass spectrometry (parent ion *m/e* 290).

In similar reactions with hydrogen bromide, only traces of solvent were collected in the trap, and it appears that the lowered volatility of the bromide fluoride precludes the use of this method. However, when hydrogen bromide was passed through a refluxing solution of *trans*-$P_3N_3F_3(NMe_2)_3$ (2·0 g) in xylene (50 ml) for 5 h the xylene solution was shown to contain the mono- and di-bromo-derivatives. After evaporation of the xylene and extraction of the residue into light petroleum the monobromide, $P_3N_3F_3Br(NMe_2)_2$, was separated from the mixture by preparative g.l.c. (5 ft column packed with 15% diethyleneglycol succinate at 130 °C) (Found: C, 13·6; H, 3·2; N, 19·9. Calc. for $P_3N_3F_3Br(NMe_2)_2$: C, 13·3; H, 3·3; N, 19·4%). The ^1H n.m.r. spectrum showed a single doublet at τ 7·27 and 7·63 (J^*_{HP} 12·5 Hz) respectively in CCl_4 and benzene, while the ^{19}F spectrum consisted of two doublets in the ratio 1 : 2 at −15·0 and −60·8 p.p.m. Attempts to bring about complete reaction by prolonged reflux or by the use of higher-boiling solvents were not successful and either decomposition or polymerization is assumed to have taken place.

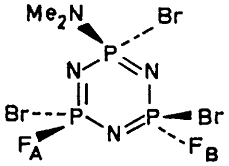
Instruments.—G.l.c. separations were carried out with an Aerograph Autoprep instrument fitted with a glass column (9 ft × $\frac{3}{8}$ in) packed with 13% dinonyl phthalate–3% silicone oil (DC 560) on 60/80 Chromosorb W. ^{19}F N.m.r. spectra were measured on either neat liquids or solutions in $CFCl_3$ (as internal standard) with a Varian HA 100 spectrometer modified by incorporating an extended locking system.

DISCUSSION

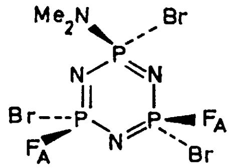
Preparations.—Dimethylamino-groups in cyclophosphazenes have been substituted by passing hydrogen halides through solutions in refluxing xylene,[10,11] but with the fluorine derivatives here, no reaction occurred with hydrogen chloride in a variety of hydrocarbons. Hydrogen bromide, a stronger nucleophile, gave both the mono- and di-bromides from $P_3N_3F_3(NMe_2)_3$ within 5 h in refluxing xylene and a sample of the former was separated by preparative g.l.c.

The hydrogen chloride reaction, however, went to completion when either a donor solvent, *i.e.*, diphenyl ether, or a solvent of moderate dielectric constant, *i.e.*, nitrobenzene was used. Mixtures of the *cis*- and *trans*-isomers of $P_3N_3Cl_2F_4$, $P_3N_3Cl_3F_3$, and $P_3N_3Cl_4F_2$ could be obtained from, respectively, $P_3N_3F_4(NMe_2)_2$, $P_3N_3F_3(NMe_2)_3$, and $P_3N_3Cl_2F_2(NMe_2)_2$ in nitrobenzene at between 150 and 190 °C. As products are removed from the reaction system in the gas stream, this approach is applicable only to the more volatile compounds. The analogous bromides could not be isolated by this method probably owing to their decomposition or polymerization at the temperatures used.

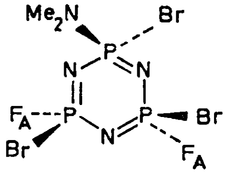
An alternative preparative method involves using the anhydrous halide in a sealed system and is generally preferable. Yields are improved and product separation is easier. There is, however, some difficulty in the HBr–$P_3N_3F_2(NMe_2)_4$ system which probably results from the necessity of brominating a geminally substituted phosphorus atom. This does not arise in the corresponding chloride system as only two, non-geminal, amine groups need be substituted in $P_3N_3F_2Cl_2(NMe_2)_2$. Support for this argument comes from ^1H and ^{19}F n.m.r. spectra of $P_3N_3F_2Br_3NMe_2$. The former shows that two isomers at least are present and from the apparent coupling constants (J^*_{HP}) of *ca.* 18·8 and 19·8 Hz the amine is present in a $PBrNMe_2$ rather than in a $PFNMe_2$ unit. The ^{19}F n.m.r. spectrum is more definitive and shows four doublets with chemical shifts between −15 and −25 p.p.m. associated with PFBr groups. All three possible isomers (a), (b), and (c) are thus present.



(a)



(b)



(c)

Except for the difluorides, the *cis–trans*-isomer mixtures which result in each case can be separated by preparative g.l.c. In contrast to the trimeric aminochlorides and -fluorides[8,9] however, the *cis*-isomer is eluted before the *trans*.

The hydrogen halide reaction probably involves initial co-ordination to the most basic ring nitrogen atom. In subsequent steps isomerization takes place as shown by the data in Table 1. As there is the possibility of isomerization catalysed by the amine hydrohalide by-product, however, it is not certain whether or not these values represent the equilibrium ratios.

^{19}F *N.m.r. Spectra.*—All the compounds give rich n.m.r. spectra owing to the complexity of the spin systems; an indication is given by that for *cis*-$P_3N_3F_3Cl_3$ (IX) shown in the Figure. The gross features however allow unambiguous assignment of structures (I)—(XII) to the compounds prepared. In general separations in the spectra of the bromide fluorides are better than for the chlorides. Chemical shift and coupling data in Table 2 are approximate and were taken from direct measurements on the spectra.

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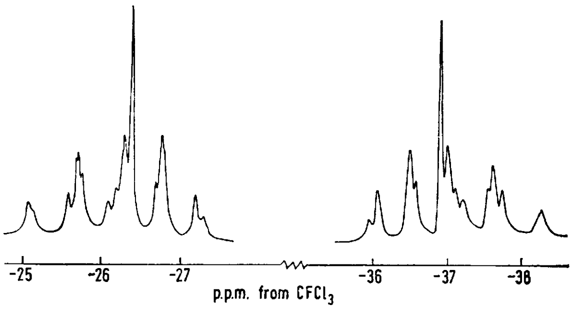
[10] G. Tesi and P. J. Slota, *Proc. Chem. Soc.*, 1960, 404.
[11] S. N. Nabi, R. A. Shaw, and C. Stratton, *Chem. and Ind.*, 1969, 166.

Compounds containing a PF_2 group show a resonance at *ca.* −70 p.p.m. split into the usual doublet by coupling to phosphorus. In the *cis*-$P_3N_3F_4X_2$ isomers (I) and (VII) the fluorines of the PF_2 group are chemically non-equivalent and two signals, incompletely separated for the chloride, are found. On the other hand the corresponding *trans*-isomers (II) and (VIII) clearly show the expected single signal in this region. There is a doublet to lower field for each of the four compounds associated with the PFCl (*ca.* −30 p.p.m.) or PFBr (*ca.* −20 p.p.m.) groups.



^{19}F N.m.r. spectrum of *cis*-$P_3N_3F_3Cl_3$ (IX)

Table 2

N.m.r. data

	δ/p.p.m.	J^*_{FP}/Hz
cis-$P_3N_3F_4Br_2$ (I)	−21·0, −69·3, −71·5	1030, 920, 950
trans-$P_3N_3F_4Br_2$ (II)	−19·0, −70·4	1020, 910
cis-$P_3N_3F_3Br_3$ (III)	−22·2	1050 [c]
trans-$P_3N_3F_3Br_3$ (IV)	−18·0 (1),[a] −20·1(2)	1010, 1020
cis-$P_3N_3F_2Br_4$ (V)	−21·2	1050
trans-$P_3N_3F_2Br_4$ (VI)	−18·9	1030
cis-$P_3N_3F_4Cl_2$ (VII)	−31·1, −70·8 [b]	970, 900
trans-$P_3N_3F_4Cl_2$ (VIII)	−30·3, −70·3	980, 900
cis-$P_3N_3F_3Cl_3$ (IX)	−31·7	1003 [c]
trans-$P_3N_3F_3Cl_3$ (X)	−30·7 [b]	980
cis-$P_3N_3F_2Cl_4$ (XI)	−31·5	980
trans-$P_3N_3F_2Cl_4$ (XII)	−29·9	980
cis-$P_3N_3F_3(NMe_2)_3$	−59·2	910
$P_3N_3F_2Br_3NMe_2$ [d]	−15·9, −18·5, −20·0, −22·3	1025, 1025, 1030, 1025

[a] Relative intensities. [b] Two overlapping signals. [c] Real $^1J_{FP}$. [d] Three isomers in mixture.

Spectra of the four trisubstituted compounds can be assigned equally readily. The *cis*-isomers (III) and (IX) with C_{3v} symmetry have equivalent fluorines and one basic doublet is observed. Two doublets for compound (IV) unambiguously indicate a *trans*-structure and although the chloride spectrum is again less well separated there is evidence for two signals.

Data for the difluorides were obtained on mixtures of isomers and as the fluorines are equivalent for each isomer, two doublets are expected. Following the trend for the tri- and tetra-fluorides, the *trans*-isomer is expected to give the lower-field signal.

There is a linear relationship between the chemical shift of the fluorine atom in a PFX group and the sum of the Pauling electronegativities of fluorine and the second halogen X, similar to that noted in phosphoryl and thiophosphoryl mixed halides.[12] The decrease from X = F (*ca.* −70 p.p.m.) to X = Cl (*ca.* −30 p.p.m.) to X = Br (*ca.* −20 p.p.m.) can be correlated with the decreased tendency for chlorine and bromine to take part in back π-bonding which leads to an increase in the magnitude of the paramagnetic screening term. In this connection it is interesting that the fluorine shift for cyclophosphazenes containing a $PFNMe_2$ group (*ca.* −60 p.p.m.) is far greater than predicted on simple electronegativity arguments. In this situation, the amine nitrogen effectively competes with fluorine for phosphorus orbitals and the π-character of the P–F bond is almost as small as when the phosphorus atom carries a second fluorine substituent.

For the *cis*-trisubstituted compounds (III) and (IX) it is possible to calculate more accurate n.m.r. parameters as these compounds belong to the $(AX)_3$ spin system which has been treated theoretically by Harris and his co-workers.[13,14] Each component of the doublets has the predicted overall quintet structure and coupling constants for the tribromide are: $^1J_{FP}$ 1050,$^2J_{PP}$ 79, and $^3J_{FP}$ *ca.* 3 Hz. Corresponding data for the trichloride are 1003, 101, and *ca.* 8 Hz.

[2/896 *Received*, 24*th April*, 1972]

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[12] A. Müller, E. Niecke, and B. Krebs, *Mol. Phys.*, 1968, **14**, 591.

[13] E. G. Finer and R. K. Harris, *J. Chem. Soc.* (*A*), 1969, 1972.

[14] R. K. Harris, J. R. Woplin, and R. Schmutzler, *Ber Bunsengesellschaft Phys. Chem.*, 1971, **75**, 134.