Reactions of Tris- and Tetrakis-dimethylaminochlorotetraphosphonitriles with Antimony Trifluoride

By **Douglas Millington** and **D. Bryan Sowerby,*** Department of Chemistry, University of Nottingham, Nottingham NG7 2RD

Three non-geminally substituted isomers of both $P_4N_4F_4(NMe_2)_4$ and $P_4N_4F_3(NMe_2)_5$ have been prepared by treating the corresponding chlorides with antimony trifluoride. The former have been separated and assigned structures (VI)—(VIII) on the basis of ^1H and ^{19}F n.m.r. spectra and g.l.c. retention time data. The tetrafluorides react further with antimony trifluoride giving three isomeric pentafluorides (IX)—(XI) by substitution of an amino-group. A mechanism is postulated for the fluorination reaction which involves the formation of an SbF_3 adduct and the possibility of isomerization as chlorine substitution takes place.

THE anionic fluorination of both hexachlorotriphosphonitrile and octachlorotetraphosphonitrile follows an exclusively geminal substitution scheme [1] and the preparation of the isomeric non-geminal chlorofluorotriphosphonitriles has only been accomplished indirectly. The method involves fluorination of chlorodimethylaminotriphosphonitriles [2] with antimony and potassium fluorides [3,4] followed by treatment with hydrogen chloride.[5] A similar investigation has been undertaken with octachlorotetraphosphonitrile with a view to establishing the relative reactivities of the two ring systems and comparing the substitution patterns involved. The reaction between octachlorotetraphosphonitrile and dimethylamine has been discussed previously;[6] in this paper we describe the fluorination of $P_4N_4Cl_4(NMe_2)_4$ and $P_4N_4Cl_3(NMe_2)_5$ with antimony trifluoride.

EXPERIMENTAL

Antimony trifluoride was recrystallised from dry methanol and stored under dry nitrogen, and all reactions were monitored by g.l.c.

Fluorination of Tetrachlorotetrakisdimethylaminotetraphosphonitrile.—The tetrachloride [6] (4·0 g, 0·008 mol) consisting of compounds (I)—(III) in approximtely equal amounts was refluxed with efficient stirring in 1,1,2-trichloroethane (200 ml) for 3 h with antimony trifluoride (1·9 g, 0·011 mol). G.l.c. showed no change in the product after this time and the mixture was treated as described previously.[3] G.l.c. examination of the separated fluorophosphonitriles showed three tetrafluorides (yield, 55%) in the ratio 33 : 25 : 18 for compounds (VI—(VIII) respectively. In addition there were three more-volatile species, later shown to be the pentafluorides (IX)—(XI), in the ratio 3 : 13 : 8. Fractional crystallization from light petroleum gave pure samples of (VI), m.p. 140°,[7] (VII), m.p. 51°, and (VIII), m.p. 109° [Found for (VI): C, 22·5; H, 5·8; N, 25·3; for (VII): C, 22·7; H, 5·0; N, 25·3; and for (VIII): C, 22·7; H, 5·8; N, 25·8. Calc. for $P_4N_4F_4(NMe_2)_4$: C, 22·2; H, 5·6; N, 25·9%].

When 1,1,2,2-tetrachloroethane was the solvent, the proportion of compounds (IX)—(XI) in the product almost doubled, but with 1,2-dichloroethane chlorine replacement was incomplete and only mixed chlorofluoroamino-compounds were produced. A reaction in trichloroethane in which the starting material contained only two [(I) and (II)] of the isomeric tetrachlorides, however, gave an unchanged final product distribution, but the geminally substituted isomer (IV), did not undergo fluorination under these conditions. When this compound was present in starting materials, both g.l.c. and mass spectrometry showed it to remain unchanged.

Fluorination of Tetrakisdimethylaminotetrafluorotetraphosphonitrile.—A sample of $P_4N_4F_4(NMe_2)_4$, containing compounds (VI)—(VIII) (2·0 g, 0·0046 mol) as obtained above was refluxed in 1,1,2,2-tetrachloroethane (200 ml) with antimony trifluoride (0·4 g, 0·002 mol) for 3 h. Treatment as before gave a viscous liquid (1·5 g, 65%) which was separated by preparative g.l.c. to give compounds (IX), m.p. 36°, (X) liquid, and (XI), m.p. 41° in the ratio 1 : 4 : 3 [Found for (IX): C, 18·3; H, 4·6; N, 24·3; for (X): C, 18·5; H, 4·9; N, 23·6; and for (XI): C, 18·2; H, 4·9; N, 24·5. Calc. for $P_4N_4F_5(NMc_2)_3$: C, 17·8; H, 4·4; N, 24·0%].

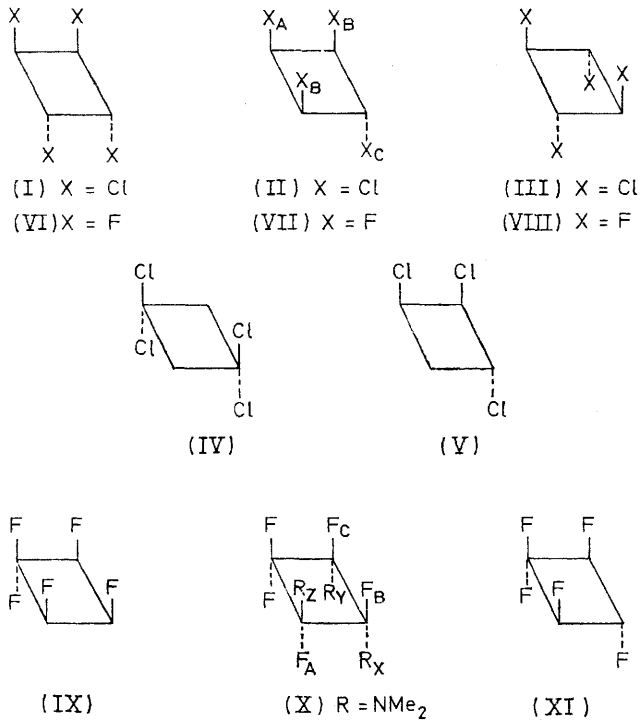
Fluorination of Trichloropentakisdimethylaminotetraphosphonitrile.—The trichloride (V) (5·1 g, 0·01 mol) and antimony trifluoride (2·0 g, 0·011 mol) were refluxed for 3 h in 1,1,2-trichloroethane (150 ml). After work-up, a viscous liquid (3·9 g) was obtained which from g.l.c. examination contained at least 14 compounds. The three tetrafluorides (VI)—(VIII) were identified but the major proportion consisted of three less volatile species in the ratio 2·5 : 5·3 : 1·0. The identity of the latter as $P_4N_4F_3(NMe_2)_5$ isomers was confirmed by separating a small amount for mass spectrometric analysis (parent ion *m/e* 457) by preparative g.l.c. Attempts to separate larger quantities by fractional crystallization, distillation, or g.l.c. were not successful probably due to the complexity of the mixture.

Instruments.—The g.l.c. apparatus has been described elsewhere.[3] Glass columns (10 ft × $\frac{3}{8}$ in) packed with 10% gum rubber or S.E. 30 stationary phases were used. N.m.r. spectra were obtained on 5% w/v solutions in carbon tetrachloride and benzene using a Varian H.A. 100 spectrometer; three samples were also examined at 220 MHz. Similar solutions were used for the ^{19}F spectra with trichlorofluoromethane as internal standard. The mass spectra were obtained on an AEI MS 902 spectrometer.

[1] J. Emsley and N. L. Paddock, *J. Chem. Soc.* (*A*), 1968, 2590.
[2] R. Keat and R. A. Shaw, *J. Chem. Soc.*, 1965, 2215.
[3] B. Green and D. B. Sowerby, *J. Chem. Soc.* (*A*), 1970, 987.
[4] B. Green, D. B. Sowerby, and P. Clare, *J. Chem. Soc.* (*A*), 1971, 3487.
[5] P. Clare, B. Green, and D. B. Sowerby, *J.C.S. Dalton*, 1972, 2374.
[6] D. Millington and D. B. Sowerby, *J.C.S. Dalton*, 1972, 2035.
[7] B. Green and D. B. Sowerby, *Inorg. Nuclear Chem. Letters*, 1969, **5**, 989.

DISCUSSION

The course of fluorination of the isomeric tetrachlorides depends strongly on the reaction temperature and although chlorine replacement is incomplete in 1,2-dichloroethane (84°), good yields of the tetrafluorides,



(Substituents omitted are NMe_2)

(VI)—(VIII), result with 1,1,2-trichloroethane (113°). In 1,1,2,2-tetrachloroethane (146°) the reaction is more complicated and gives in addition substantial quantities of the pentafluorides, (IX)—(XI), thus showing the possibility of substituting dimethylamino-groups attached to phosphorus by antimony trifluoride. Mass spectral evidence during the course of the reaction confirms that, although amine substitution is much less probable than chlorine substitution, significant amounts of chloride-fluorides containing three dimethylamino-groups are produced. This mode of reaction for antimony trifluoride is new,[8] and contrasts with the only other report of its reaction with an amino-compound in which $PhN{=}P(NEt_2)Cl_2$ is converted by cleavage of the phosphazo-bond into Et_2NPF_4.[9] The final state of combination of the antimony has not been determined but is likely to involve chlorodimethylamino-species or their reorganization products.

The data also indicate that as fluorination proceeds the reaction becomes increasingly difficult, in agreement with the postulated mechanism[3] which requires the initial formation of an SbF_3 addition compound with the phosphonitrile *via* a lone pair of electrons on a ring nitrogen atom. As fluorination proceeds, the basicity of the ring nitrogen atoms is reduced and adduct formation progressively less favoured. It is a significant indication of the basicities of tetramers substituted by dimethylamino-groups however that at least five fluorine atoms may be introduced by this method.

G.l.c. Behaviour.—The g.l.c. behaviour of the tetrameric fluorides parallels that of the chlorides[6] but the increased volatility of the former improves both the separation of isomers and the efficiency of their collection. Table 1 lists the retention times of compounds (VI)—(XI) under standardized conditions. As previous results for the amino-chlorides showed an increase in retention time with the number of pairs of 1,3-*cis*-amino-groups,[6] preliminary structure assignments may be made as shown for compounds (VI)—(XI). It should be noted that while the fluorides (VI) and (VII) are just separable, the analogous chlorides, (I) and (II), were always eluted as a single peak.

^1H *N.m.r. Spectra.*—Chemical shifts and apparent coupling constants for compounds (VI)—(XI) are summarized in Table 1. The tetrafluorides (VI)—(VIII) all show a basic doublet in carbon tetrachloride each component of which is split by fluorine-proton coupling[10] into a further doublet. This confirms that the compounds all have non-geminal structures. The benzene spectra of compounds (VI) and (VIII) are almost identical but for compound (VII) the appearance of two doublets in the ratio 1 : 3 implies non-equivalent amine groups

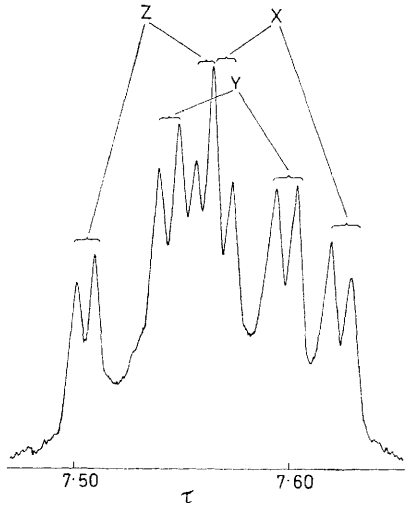


FIGURE 1 ^1H N.m.r. spectrum of $P_4N_4F_5(NMe_2)_3$ (X) at 220 MHz in benzene solution

and the 1,*cis*-3,*trans*-5,*cis*-7-structure is assigned. It is not possible with this data to confirm the structures suggested for (VI) and (VIII) by the g.l.c. data but single-crystal *X*-ray determinations[11,12] have established them.

[8] P. Clare, D. Millington, and D. B. Sowerby, *Chem. Comm.*, 1972, 324.

[9] M. Bermann and J. R. Van Wazer, *Angew. Chem. Internat. Edn.*, 1971, **10**, 733.

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

[11] D. Millington, T. J. King, and D. B. Sowerby, *J.C.S. Dalton*, 1973, 396.

[12] M. J. Begley, T. J. King, D. Millington, and D. B. Sowerby, unpublished results.

The spectra of compounds (IX)—(XI) in benzene solution are well resolved and compound (X) may be uniquely assigned the structure in which all the amine groups are non-equivalent. The spectrum shown in Figure 1 clearly shows three doublets, each exhibiting proton–fluorine coupling. For assignments to the other two pentafluorides it is necessary to consider the magnitude of the benzene solvent shifts ($\Delta\tau$). In related trimeric [13] and tetrameric [6] compounds, the largest value has been associated with a *cis*-arrangements of amine substituents and here the structure with three *cis*-amine groups is assigned to compound (IX).

The broad, unresolved peak which has often been noted in ^{1}H n.m.r. spectra of amine substituted phosphonitriles appears in many of the spectra. It is more distinct in the symmetrically substituted tetrakis-isomers [(I), (III), (VI), and (VIII)] than in the trisdimethylamino-compounds and is likely to be associated with the presence of chemically equivalent but magnetically non-equivalent protons. The long range proton–proton coupling though small is not likely to be negligible,[14] and significant effects are to be expected in situations where the amine groups become more nearly equivalent.

^{19}F *N.m.r. Spectra.*—These data are summarized in Table 1 and the structure assigned to compound (VII) is confirmed by the presence of three doublets in the fluorine spectrum (see Figure 2). A useful correlation can be drawn between the position of the fluorine resonance and substituent orientation within a molecule by comparing data for compounds (VI) and (VIII) and for a number of pairs of related trimeric compounds,[3,4] *i.e. cis*- and *trans*-$P_3N_3Cl_2F_2(NMe_2)_2$, *cis*- and *trans*-$P_3N_3F_3(NMe_2)_3$, and *cis*- and *trans*-$P_3N_3F_2(NMe_2)_4$. Resonance in (VI) is *ca.* 3 p.p.m. to low field of that in (VIII) while the *cis*-isomers of the trimeric compounds also resonate to low field of the *trans*-isomers. Thus a fluorine atom *cis* to a dimethylamino-group on an adjacent phosphorus atom resonates to high field of a fluorine *cis* to other fluorine substituents; amine groups on more distant phosphorus atoms are likely to have only a small effect on the resonance position. For compound (VII), therefore, the highest field resonance may be related to F_C and that at lowest field to F_A.

TABLE 1

G.l.c. and n.m.r. data

Compound	Retention time / min	^{1}H n.m.r. data					^{19}F n.m.r. data	
		τ(CCl_4)	J^*_{HP} [a] (CCl_4)	τ(C_6H_6)	J^*_{HP} [a] (C_6H_6)	$\Delta\tau$	δ [d]	J^*_{FF}/Hz
(VI)	14·7	7·28	11·4	7·44	11·0	+0·16	−58·8	870
(VII)	14·3	7·28	11·4	7·41(1) [b]	11·6	+0·13	−55·4(1) [b]	870
				7·45(3)	11·7	+0·17	−58·3(2)	880
							−60·0(1)	840
(VIII)	10·7	7·28	11·5	7·43	11·4	+0·15	−61·5	830
(IX) [c]	5·7	7·249	12·0	7·564(1)	12·4	+0·315	−57·9(1)	920
				7·616(2)	12·3	+0·367	−59·6(2)	920
							−69·2(2)	870
(X) [c]	5·0	7·253	12·2	7·538(1)	12·3	+0·285	−58·9(1)	950
				7·575(1)	12·3	+0·322	−61·2(1)	920
				7·604(1)	12·3	+0·351	−62·2(1)	910
							−69·2(2)	920
(XI) [c]	4·5	7·249	12·6	7·515(1)	12·3	+0·266	−62·4(2)	870
				7·593(2)	12·3	+0·344	−63·8(1)	840
							−69·3(1)	870
							−70·5(1)	870

[a] In addition all show $^4J^*_{HF}$ coupling of *ca.* 2 Hz. [b] Relative intensities in parentheses. [c] ^{1}H n.m.r. measurements at 220 MHz. [d] In p.p.m. from $CFCl_3$.

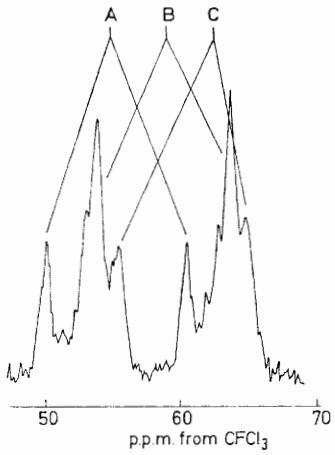


FIGURE 2 ^{19}F N.m.r. spectrum of $P_4N_4F_4(NMe_2)_4$ (VII)

Four doublets in a ratio 2 : 1 : 1 : 1 in the spectrum of compound (X) (see Figure 3) confirm the assigned structure as the three unit intensity signals are in the region characteristic of $PF(NMe_2)$ groups. The two non-geminal fluorine signals for compound (IX) are to low field of those for (XI) suggesting that in the former the fluorine atoms are *cis* to other fluorines on adjacent phosphorus atoms. Further, the signal at lowest field for compound (XI) has an intensity of two in agreement with the proposed structure.

[13] R. Keat and R. A. Shaw, *J. Chem. Soc.* (*A*), 1968, 703.
[14] E. G. Finer, R. K. Harris, M. R. Bond, R. Keat, and R. A. Shaw, *J. Mol. Spectroscopy*, 1970, **33**, 71.

For all three isomers, the fluorines in the PF_2 group are non-equivalent and two signals are expected. This is in fact observed only for compound (XI). It is perhaps not unexpected for compound (X) as non-equivalence arises solely from the orientation of a fluorine atom six bonds distant but this certainly is not the case for compound (IX).

Reaction Mechanism.—The first step in the proposed mechanism is the formation of phosphonitrile–antimony trifluoride addition compound involving co-ordination at the ring nitrogen atom of greatest basicity. In partially substituted triphosphonitriles [15] such basicities can be assessed with considerable accuracy by considering contributions from substituents on adjacent and distant

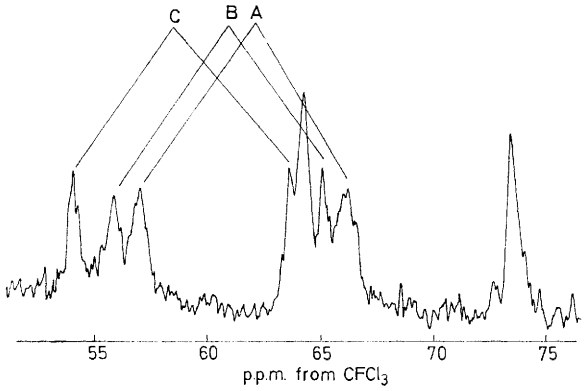


FIGURE 3 ^{19}F N.m.r. spectrum of $P_4N_4F_5(NMe_2)_3$ (X)

phosphorus atoms. Extension to the tetrakisdimethylamino-compounds (I)—(IV) would imply similar basicities for each compound due to contributions from two amine groups on adjacent and two on distant phosphorus atoms. It is clear from the lack of reactivity of the geminal isomer (IV) that this approach to basicity and thus reactivity is not completely valid. The problem arises due to the different base strengthening effects of, on the one hand, two $PCl(NMe_2)$ groups and on the other one $P(NMe_2)_2$ and one PCl_2 group. In amine substituted compounds, base strengthening in general arises from an increased localization of the sp^2 lone pair on a ring nitrogen due to exocyclic π-bonding from the amine nitrogen lone-pair. The extent of such delocalization is clearly dependent on the second substituent X in a $PX(NMe_2)$ unit and will be reduced if X itself tends to form π-bonds to phosphorus. Thus for $X = NMe_2$, the overall base strengthening will be lower than when the amino-groups are on different phosphorus atoms and the lack of reactivity of (IV) may be rationalised on this basis.

The production of tetrafluorides in a substantially constant ratio [1·6 : 1·4 : 1 for (VI), (VII), (VIII)] implies that isomerization occurs during the reaction. This is certainly shown by the formation of the 1,*trans*-3,*cis*-5,*trans*-7-tetrafluoride (VIII) from a chloride mixture containing only compounds (I) and (II). No isomerization occurs for the chlorides on prolonged reflux in any of the chlorinated ethane solvents, thus inversion of configuration must occur as substitution proceeds. However, the reaction can proceed neither with complete inversion nor with complete retention of phosphorus configuration or the product isomer ratio would be identical to that in the starting material.

As an approach to this problem, reaction is considered to take place initially at phosphorus atoms adjacent to the most basic nitrogen atom(s) and that there is an equal probability that the substitution step involves retention or inversion. On this basis, it is possible to calculate the isomer ratio in products; some results are

TABLE 2

Isomer ratios

Starting material	Predicted ratio (%)	Observed ratio (%)
cis- or *trans*-$P_3N_3Cl_3(NMe_2)_3$ [a]	25 : 75 [b]	5 : 95 [b]
$P_4N_4Cl_3(NMe_2)_5$ (V)	25 : 50 : 25	28 : 61 : 11
$P_4N_4Cl_4(NMe_2)_4$ (I)—(III)	25 : 50 : 12·5 : 12·5 [c]	44 : 32 : 24 : 0 [c]

[a] Ref. 4. [b] *cis* : *trans* ratio. [c] Ratio of: (VI) : (VII) : (VIII) : 1,*cis*-3, *cis*-5, *cis*-7 isomer

shown in Table 2. It is significant that, as found experimentally, the predicted product ratios are independent of the isomer ratio in the starting material. Agreement between the predicted and observed product ratios is not exact but this is not unreasonable as there are likely to be factors operative which upset the randomness of the substitution steps. This could arise because of the nature of the SbF_3 adduct formed; the three-dimensional structure of the fluoride [16] may indeed lead to interaction with $(SbF_3)_n$ units rather than a discrete molecular species thus favouring either retention or inversion. Experimentally there is certainly a tendency to favour the formation of *trans*-isomers and steric factors may impose a preferred configuration at phosphorus. Discrepancies between the predicted and experimental distributions are related to the number of possible isomerization steps and suggest that any effects leading to the formation of a preferred isomer are cumulative.

We thank Dr. A. F. Childs (Albright and Wilson Ltd.) for a gift of $P_4N_4Cl_8$, Mr. M. A. Healy for help in obtaining many of the spectra, and the S.R.C. for the award of a studentship (to D. M.) and for the 220 MHz spectra.

[3/1113 *Received*, 30*th May*, 1973]

[15] D. Feakins, W. A. Last, S. N. Nabi, and R. A. Shaw, *J. Chem. Soc.* (*A*), 1966, 1831.
[16] A. J. Edwards, *J. Chem. Soc.* (*A*), 1970, 2751.