Reaction of Octakis(dimethylamino)tetraphosphonitrile with Antimony Trifluoride

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

A series of 14 non-germinally substituted dimethylaminofluorotetraphosphonitriles, $P_4N_4F_n(NMe_2)_{8-n}$ where n = 1,2(four isomers), 3(three isomers), 4(three isomers), and 5(three isomers), has been prepared by the reaction of $P_4N_4(NMe_2)_8$ with antimony trifluoride. The tetra- and penta-fluorides are identical with those obtained from the fluorination of $P_4N_4Cl_4(NMe_2)_4$ but five new compounds have been separated and assigned structures from g.l.c., ^1H and ^{19}F n.m.r. data. The reaction mechanism is thought to be similar to that discussed previously and involves co-ordination of antimony trifluoride to the most basic ring nitrogen atom rather than to an amine substituent. Fluorination follows a non-geminal path with a tendency to form larger amounts of *trans*- rather than *cis*-isomers.

NON-GEMINALLY substituted dimethylaminofluoro-derivatives of both tri- and tetra-phosphonitriles have been obtained from the corresponding chlorides by treatment with antimony trifluoride.[1-3] Here an alternative preparative route[4] to the tetrameric compounds is described which involves the replacement of dimethylamino-groups in $P_4N_4(NMe_2)_8$ by reaction with antimony trifluoride.

EXPERIMENTAL

Octakis(dimethylamino)tetraphosphonitrile was prepared by heating the octachloride in refluxing n-hexane with an excess of dimethylamine for a prolonged period;[5] antimony trifluoride was recrystallized from dry methanol. All reactions were monitored by g.l.c.

Reaction in 1,2-*Dichloroethane.*—Octakis(dimethylamino)-tetraphosphonitrile (3·0 g, 0·006 mol) was refluxed for 3 h with antimony trifluoride (3·0 g, 0·017 mol) in 1,2-dichloroethane (150 ml). The reaction mixture examined by g.l.c. contained three compounds in the ratio 1 : 17 : 10 with relative retention times of 1 : 0·68 : 0·43. The solvent was evaporated and the residue was refluxed for *ca.* 2 h with light petroleum (b.p. 60—80°) to which a few drops of water had been added. After filtration the solution was dried ($CaCl_2$); g.l.c. analysis now indicated the compounds to be present in the ratio 1 : 2·2 : 0·2. Mass spectrometry showed that the compound with the longest retention time was starting material and that with the shortest retention time was $P_4N_4F_2(NMe_2)_6$. The intermediate compound was separated by preparative g.l.c. and shown to be pure heptakis(dimethylamino)fluorotetraphosphonitrile (I) (48% yield), m.p. 167° [Found: C, 33·7; H, 8·8; N, 30·0. Calc. for $P_4N_4F(NMe_2)_7$: C, 33·1; H, 8·3; N, 30·4%]. Similar reactions with a large excess of antimony trifluoride and/or prolonged reflux times gave similar product distributions but lower overall yields.

Reaction in 1,1,2-*Trichloroethane.*—The phosphonitrile (3·0 g, 0·006 mol) was refluxed for 5 h with antimony trifluoride (4·2 g, 0·023 mol) in 1,1,2-trichloroethane (150 ml). Treatment as before gave a viscous liquid (2·4 g) which showed two major g.l.c. peaks in the ratio 1 : 3 with retention times of 11·1 and and 10·3 min respectively. Separation of these by preparative g.l.c. and mass spectrometry showed both peaks to be associated with $P_4N_4F_2(NMe_2)_6$ species. By ^{19}F n.m.r. spectrometry (see later) the less-volatile material was identified as compound (II) while the fraction with the shorter retention time was probably a mixture of the three isomers (III), (IV), and (V). The total conversion into difluorides was 73%. Mass spectrometry of the crude reaction product showed the presence of small amounts of the monofluoride and more highly fluorinated compounds. With increased amounts of antimony trifluoride and longer periods of reflux the results were similar to those described above but slightly increased amounts of the higher fluorides were produced.

Reaction in 1,1,2,2-*Tetrachloroethane.*—A reaction of the phosphonitrile (2·7 g, 0·005 mol) with antimony trifluoride (1·1 g, 0·006 mol) in tetrachloroethane (150 ml) gave a

[1] B. Green and D. B. Sowerby, *J. Chem. Soc.* (*A*), 1970, 987.
[2] B. Green, D. B. Sowerby, and P. Clare, *J. Chem. Soc.* (*A*), 1971, 3487.
[3] D. Millington and D. B. Sowerby, *J.C.S. Dalton*, 1973, 2649.
[4] P. Clare, D. Millington, and D. B. Sowerby, *J.C.S. Chem. Comm.*, 1972, 324.
[5] R. Keat and R. A. Shaw, *J. Chem. Soc.* (*A*), 1966, 908.

colourless liquid (1·9 g). G.l.c. and mass spectrometry confirmed the presence of di- and tetra-fluorides (12 and 6% respectively) but the bulk of the product consisted of three isomers in the approximate ratio of 1 : 5 : 3 with retention times of 8·1, 7·3, and 6·5 min respectively. After g.l.c. separation, mass spectrometry confirmed compounds (VI) (m.p. 33°), (VII) (m.p. 54°), and (VIII) (m.p. 41°) as isomeric trifluorides, $P_4N_4F_3(NMe_2)_5$ [Found for compound (VII): C, 26·1; H, 6·6; N, 27·2. Calc. for $P_4N_4F_3(NMe_2)_5$: C, 26·3; H, 6·6; N, 27·1%].

With 2 mol of antimony trifluoride, the bulk of the product (85%) consisted of three isomeric tetrafluorides identified by comparison with the products obtained from the fluorination of $P_4N_4Cl_4(NMe_2)_4$.[3] In addition, 13% of the trifluorides (VI)—(VIII) was obtained.

Prolonged reflux with an excess of antimony trifluoride gave as the major proportion of the product the three pentafluorides isolated previously.[3]

Complex Formation.—A solution of antimony trichloride (0·52 g, 0·002 mol) in ether (50 ml) was added dropwise to a refluxing solution of octakis(dimethylamino)tetraphosphonitrile (1·0 g, 0·002 mol) in ether (100 ml) until a white precipitate started to form. The clear solution was decanted under a nitrogen atmosphere, evaporated to dryness, and the remaining solid extracted with light petroleum to remove any unchanged aminophosphonitrile. A white solid (0·76 g) remained which decomposed on exposure to the atmosphere [Found: C, 19·8; H, 4·4; Cl, 21·7; N, 16·5. Calc. for $P_4N_4(NMe_2)_8,2SbCl_3$: C, 19·4; H, 4·9; Cl, 21·6; N, 17·0%]. Major bands in the i.r. spectrum occurred at: 1315s, 1285s, 1222w, 1185s, 1065m, 985vs, 748sh, 740s, 727w, 670m, and 634m cm^{-1}.

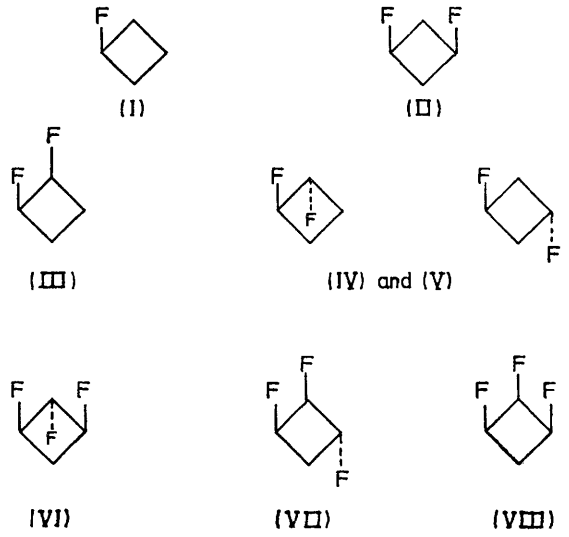
In a similar reaction a solution of antimony trifluoride (0·34 g, 0·002 mol) in methanol (30 ml) gave a moisture-sensitive, insoluble residue which had an analysis close to that expected for $P_4N_4(NMe_2)_8,4SbF_3$ [Found: C, 15·5; H, 4·7; N, 13·3. Calc. for $P_4N_4(NMe_2)_8,4SbF_3$: C, 15·4; H, 3·8; N, 13·5%].

Instruments.—The g.l.c. apparatus has been described elsewhere.[1] ^1H N.m.r. spectra were obtained on 5% (w/v) solutions in carbon tetrachloride and benzene using a Varian HA 100 spectrometer; three samples were also examined at 220 MHz. ^{19}F N.m.r. spectra were measured with trichlorofluoromethane as internal standard and mass spectra were obtained using an A.E.I. MS902.

DISCUSSION

Structural Assignments.—Although the structure of compound (I) is unambiguously established by analysis and mass spectrometry, a number of points arise from both the ^1H and ^{19}F n.m.r. spectra. The 220 MHz proton spectrum of a carbon tetrachloride solution clearly separates the signal due to the non-geminal amine group, but there is only a broad doublet for the remaining six amine groups (see Table 1). In benzene solution, the latter is split into two doublets with that at higher field being tentatively associated with the three groups *trans* to the fluorine atom.[5,6] The ^{19}F spectrum (see Table 2) consists of a doublet at −59·9 p.p.m. from $CFCl_3$ each component of which is split by *ca.* 12 Hz.

The two $P_4N_4F_2(NMe_2)_6$ fractions separated by g.l.c. from the reaction in trichloroethane give markedly different ^{19}F n.m.r. spectra. That with lower retention shows three doublets while only a simple doublet appears for the less-volatile fraction. As all possible



(Substituents omitted are NMe_2 groups)

TABLE 1

^1H N.m.r. spectra

Compound	τ(CCl_4)	J^*_{HF}(CCl_4)	τ(C_6H_6)	J^*_{HF}(C_6H_6)
(I) [a]	7·314(1) [b]	11·2 [c]		
	7·448(6)	10·2	*d*	
			7·338(3)	10·0
			7·359(3)	9·8
(II)	7·30(1)	11·6 [c]	7·36(1)	11·4 [c]
	7·43(1)	11·3	7·39(1)	11·2
	7·44(1)	11·5	7·42(1)	10·7
(VI)	7·30(3)	11·6 [c]	7·37(1)	11·8 [c]
			7·42(2)	11·4 [c]
	7·43(2)	11·0	7·40(1)	11·2
			7·47(1)	11·0
(VII) [a]	7·291(3)	11·6 [c]	7·367(1)	11·8 [c]
			7·390(1)	12·2 [c]
			7·409(1)	12·1 [c]
	7·437(2)	11·6	7·424(1)	11·3
			7·435(1)	11·3
(VIII) [a]	7·294(3)	11·6 [c]	7·364(1)	12·0 [c]
			7·390(2)	12·0 [c]
	7·426(1)	11·4	7·394(1)	11·0
	7·436(1)	11·2	7·480(1)	11·0

[a] Measurements at 220 MHz. [b] Relative intensities in parentheses. [c] In addition coupling due to $^4J^*_{HF}$ is observed. [d] Not measurable from spectrum.

TABLE 2

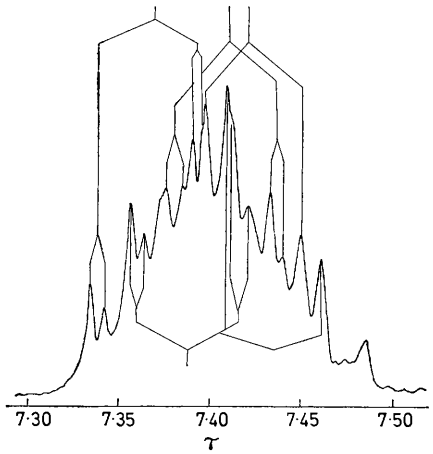
^{19}F N.m.r. spectra

Compound	δ [a]	J^*_{FP}
(I)	−59·9	910
(II)	−59·5	900
(III) [b]	−59·1	920
(IV) and (V) [b]	−60·4	910
	−61·4	870
(VI)	−61·4(2) [c]	870
	−62·9(1)	850
(VII)	−58·1(1)	880
	−59·6(1)	840
	−60·8(1)	830

[a] In p.p.m. upfield from $CFCl_3$. [b] From a mixture of isomers. [c] Relative intensities in parentheses.

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

isomers of this stoicheiometry possess equivalent fluorine atoms, the first fraction is a mixture of three isomers but the latter is a single species. The resonance position implies that all four compounds are non-geminally substituted. The proton data support this assignment and for compound (II) three doublets are observed. Two of these can be associated with the $P(NMe_2)_2$ groups, as they show no four bond proton–fluorine coupling, and it is possible to exclude on this basis the 1, *trans*-5-structure. The longer retention time of this compound suggests that the amines of the $PF(NMe_2)$ groups occupy *cis*-positions [3,6] and tentatively the 1,*cis*-5-structure is assigned. This is supported by the position of the fluorine resonance as fluorine atoms flanked in *cis*-positions by dimethylamino-groups resonate to high field of those flanked by other fluorine atoms.[3] On this basis it is possible to associate the lowest field signal (−59·1 p.p.m.) from the mixture of the three isomers with the 1, *cis*-3-compound (III).



^{1}H N.m.r. spectrum of $P_4N_4F_3(NMe_2)_5$ (VII) in benzene solution at 220 MHz

Both the position of the ^{19}F resonances and the observation of four bond proton–fluorine coupling for three amine groups in the ^{1}H n.m.r. spectra indicate that the three trifluorides (VI)—(VIII) are non-geminal isomers. Further the structure of (VII) follows unambiguously from the presence of five overlapping doublets in the ^{1}H spectrum of a benzene solution (see Figure) and three doublets in the ^{19}F spectrum. G.l.c. retention time data allow tentative assignments of structures (VI) and (VIII) to the other two isomers the former being supported by the ^{19}F signal occurring at *ca.* 61 p.p.m. as would be predicted from the data for compound (VII) for a '*cis–trans–cis*' arrangement of fluorine substituents.

Course of the Reaction.—This method of fluorination represents a new route to dimethylaminofluorotetraphosphonitriles and by controlling the quantity of antimony trifluoride used and the reaction temperature it is possible to obtain good yields of compounds with the stoicheiometries $P_4N_4F_n(NMe_2)_{8-n}$ (n = 1—5). It is interesting that the monofluoride can be readily obtained by this method in contrast to the difficulties which attend the preparation of the analogous monochloride.[6] A further advantage from this approach is the small number of possible intermediates (compared with the possibility of producing mixed chlorofluoroamines using the alternative method [3]) which simplifies purification problems.

The isomer distribution within the tetra- and pentafluoride stoicheiometries in these experiments is almost identical to that observed in the preparation of these compounds from the corresponding aminochlorophosphonitriles [3] suggesting that a broadly similar mechanism is applicable. This would involve the formation of an adduct with antimony trifluoride which is not unreasonable as $P_4N_4(NMe_2)_8$ is known to be a strong base.[7] Indeed there is chemical evidence (see Experimental section) for such a species although the data are not yet complete on account of solubility problems. However, a 1 : 2 adduct has been isolated with the more-soluble antimony trichloride as acceptor. That $P_4N_4(NMe_2)_8$ is held during the reaction as either an insoluble or involatile species is shown by the large increase in the proportion of this compound when the $P_4N_4F(NMe_2)_7$ reaction mixture is processed. As the octa-amine is the most basic phosphonitrile present, before work-up it is likely to be held almost entirely in the form of an insoluble adduct. Thus it would not be detected then by g.l.c. but would show in its true concentration after treatment with water in the work-up procedure. An entirely similar situation is found during the isolation of $P_3N_3F(NMe_2)_5$ from the SbF_3–$P_3N_3(NMe_2)_6$ reaction.[8]

There is, in the absence of crystallographic data, some doubt about the position of co-ordination to the phosphonitrile as both the ring nitrogen atoms and the amine group substituents are basic sites. This may be partially resolved in favour of the former by considering the formation of the isomeric difluorides (II)—(V). Evidence from both g.l.c. and ^{19}F n.m.r. spectroscopy indicates that approximately equal quantities of the four possible non-geminal isomers are formed and this can be readily rationalized if attack takes place at a ring nitrogen atom. After substitution of the first amine group, attack by SbF_3 is directed to the ring atoms flanked by $P(NMe_2)_2$ groups as these are more highly basic than those flanked by a $PF(NMe_2)$ group and equal amounts of 1,3- and 1,5-disubstitution products would be expected. Attack *via* an amine substituent, on the other hand, would make 1,3-substitution twice as likely as 1,5-substitution and is thus not the favoured mechanism.

Adduct formation *via* a ring nitrogen atom necessarily leads to a non-geminal replacement scheme as introduction of a fluorine atom lowers the basicity of the flanking ring nitrogens and further attack takes place across the ring. This is in agreement with experiment

[7] D. Feakins, W. A. Last, and R. A. Shaw, *J. Chem. Soc.*, 1964, 4464.

[8] P. Clare and D. B. Sowerby, *J. Inorg. Nuclear Chem.*, in the press.

as species containing PF_2 groups were not isolated until it was necessary in the $P_4N_4F_5(NMe_2)_3$ isomers.

If the substitution process is considered to take place *via* attack at the most basic ring nitrogen atom, the ratio of the isomers for a given stoicheiometry can be predicted, and these together with the observed values are given in Table 3. In a similar treatment

TABLE 3

Isomer ratios

Stoicheiometry	Predicted	Observed
$P_4N_4F_2(NMe_2)_6$	25 : 25 : 25 : 25 [a]	25 : 25 : 25 : 25
$P_4N_4F_3(NMe_2)_5$	25 : 50 : 25 [b]	35 : 54 : 11
$P_4N_4F_4(NMe_2)_4$	25 : 50 : 12·5 : 12·5 [c]	43 : 33 : 24 : 0
$P_4N_4F_5(NMe_2)_3$	25 : 50 : 25 [c]	38 : 50 : 12

[a] Ratio of (II) : (III) : (IV) : (V). [b] Ratio of (VI) : (VII) : (VIII). [c] Ref. 3.

presented earlier [6] for data on the fluorination of chlorodimethylaminotetraphosphonitriles, it was necessary to postulate that in the chlorine substitution step there was an equal probability of retention or inversion of the configuration at the phosphorus atom. In the present case this is not necessary, though it may occur, as the entering fluorine atom could displace either of the dimethylamino-groups and in the simplest approach equal amount of *cis*- and *trans*-isomers would result. This is found for the difluoride step but the discrepancies between predicted and experimental ratios become larger for higher degrees of substitution. Clearly here there is the same tendency towards the formation of *trans*-isomers as was found in the chloride-substitution experiments and similar factors are likely to be operative.

Analogous reactions occur with $P_3N_3(NMe_2)_6$ but much more forcing conditions are required.[4,8] This is rather surprising as the basicity [7] is only slightly lower than that of the tetramer and chlorodimethylaminotriphosphonitriles can be fluorinated by SbF_3 with ease.[1,2] An explanation probably lies in the lack of flexibility of the trimeric ring and the bulkiness of the amino-groups both of which would inhibit ready formation of the initial addition compound.

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 n.m.r. spectra.

[3/1790 *Received*, 29*th August*, 1973]