Fluorination of Dimethylaminopentachlorocyclotriphosphazene

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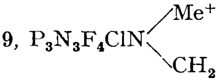
Reaction of dimethylaminopentachlorocyclotriphosphazene (I) with KSO_2F under reduced pressure yields a series of partially fluorinated compounds, $P_3N_3F_nCl_{5-n}NMe_2$ (n = 1—4). For n = 1 and 3, *cis* and *trans* isomers are formed. The reaction is shown to follow a geminal replacement scheme with preferential attack at the PCl_2 group. Reaction of (I) with KSO_2F in $MeNO_2$ yields mainly $P_3N_3F_5NMe_2$ while with NaF in MeCN solution the major product is $P_3N_3F_4ClNMe_2$. A second monofluoride, $P_3N_3FCl_4NMe_2$, in which the fluorine is attached to the amine substituted phosphorus atom is obtained by reacting (I) with SbF_3 in the presence of $SbCl_5$. Structures are proposed on the basis of ^1H and ^{19}F n.m.r. spectroscopy. Important features from i.r. spectroscopy and mass spectrometry are also discussed.

THE fluorination of chlorocyclophosphazenes partially substituted by dimethylamino-groups is of interest as earlier work has shown that the position of fluorination depends upon the fluorinating agent used. Reactions with bis-, tris-, and tetrakis-dimethylamino-derivatives have been reported[1,2] while reactions of the monodimethylamino-derivative, $P_3N_3Cl_5NMe_2$ (I) are described here.

EXPERIMENTAL

Reaction of $P_3N_3Cl_6$ *with Two Moles of Dimethylamine*.—This reaction was carried out as described by Keat and Shaw.[3] G.l.c. analysis of the reaction product showed the presence of $P_3N_3Cl_6$ (6%), $P_3N_3Cl_5NMe_2$ (91%), *trans*-$P_3N_3Cl_4(NMe_2)_2$ (3%), and *cis*-$P_3N_3Cl_4(NMe_2)_2$ (trace). If an excess of 10% over the stoicheiometric amount of dimethylamine was used the proportion of $P_3N_3Cl_5NMe_2$ (89%) was not increased and more of the bisdimethylamino-derivatives (8%) were produced. Samples of pure $P_3N_3Cl_5NMe_2$ (b.p. 158°, 16 mmHg) were obtained by distillation or by preparative scale g.l.c. (5 ft. column containing 15% silicone oil DC560 at 202°).

Reaction of Compound (I) *with Sodium Fluoride*.—A solution of (I) (5·0 g, 0·014 mol) in refluxing MeCN (50 ml) was stirred vigorously with NaF (14·8 g, 0·35 mol). After 6 h an aliquot portion was removed for g.l.c. analysis which showed that no reaction was occurring. At this stage, 5 drops of 40% aqueous HF were added to the contents of the reaction flask and heating was continued for a total of 20 h. Insoluble materials were filtered off, washed with a little MeCN (*ca.* 10 ml), and the filtrate and combined washings distilled at atmospheric pressure. G.l.c. analysis of the distillate showed the presence of two compounds apart from the solvent. A sample of the compound with the shorter retention time (10% abundance) was separated by g.l.c. and shown by i.r. spectroscopy to be $P_3N_3F_5NMe_2$ (VIII).[4,5] A sample of the second component (VII) (90% abundance) was obtained by preparative g.l.c. (10 ft. column containing 15% silicone oil SE 30 at 109°) (Found: C, 8·3; H, 2·1; N, 19·3. Calc. for $P_3N_3F_4ClNMe_2$: C, 8·2; H, 2·1; N, 19·2%). I.r. absorptions: 3005w, 2958mw, 2920mw, 2890mw, 2855w, 2810w, 1482mw, 1460mw, *ca.* 1450sh, *ca.* 1300sh, 1263vs, 1208vw ,1161m, 1105w, 1063mw, 1018m, 1000ms, 980m, 940ms, 916s, 834s, 780vvw, 752ms, 718m, 588ms, 514ms, 483m, 465ms cm^{-1}. Mass spectrum (only phosphorus containing ions of monoisotopic intensity >5% of the base peak are included): *m/e* 290, $P_3N_3F_4ClNMe_2^+$(23%); 289,  $P_3N_3F_4ClN\genfrac{}{}{0pt}{}{\diagup Me^+}{\diagdown CH_2}$ (7%); 247, $P_3N_3F_4ClH^+$ (8%); 246, $P_3N_3F_4Cl^+$ (98%); 212, $P_3N_3F_4H^+$ (100%); 211, $P_3N_3F_4^+$ (18%); 167, $P_2N_2F_4H^+$ (17%); 166, $P_2N_2F_4^+$ (7%); 114, $P_2NF_2^+$ (7%); and 69, PF_2^+ (13%).

The residue remaining in the reaction flask (1·2 g) was extracted with hot n-hexane. A polymeric residue (0·75 g) remained. G.l.c. analysis of the extracted material showed the presence of $P_3N_3F_4ClNMe_2$, unreacted $P_3N_3Cl_5NMe_2$ and small amounts of compounds with intermediate retention times which are probably due to less fluorinated species.

Reaction of Compound (I) *with Potassium Fluorosulphite in Nitromethane*.—Potassium fluorosulphite was prepared by shaking dried KF (40 g, 0·69 mol) with an excess of SO_2 (100 g, 1·56 mol) in a steel bomb for 96 h. The increase in weight (16·8 g) corresponded to a 56% conversion.

A solution of (I) (5·0 g, 0·014 mol) in refluxing nitromethane (50 ml) was vigorously stirred with an excess of the KSO_2F–KF mixture (20 g). After 5 h an aliquot portion was removed from the reaction mixture and shown by g.l.c. to contain no unreacted $P_3N_3Cl_5NMe_2$ and the reaction was stopped. The insolubles were removed by filtration, washed with nitromethane (20 ml), and the washings added to the filtrate. G.l.c. analysis of the filtrate indicated the presence of two compounds which were identified on the basis of retention times as $P_3N_3F_5NMe_2$ (VIII) (85%) and $P_3N_3F_4ClNMe_2$ (VII) (15%). Distillation using a fractionating column at atmospheric pressure yielded a solution of $P_3N_3F_5NMe_2$ (98% purity) in $MeNO_2$ but it was not possible to separate the pentafluoride from solvent by distillation alone and the reaction was not further investigated.

Reaction of Compound (I) *with* KSO_2F *under Reduced Pressure*.—A slurry of (I) (28·8 g, 0·08 mol) with the KSO_2F–KF mixture (35·1 g) was placed in a 250 ml round-bottomed flask which was connected to a cold trap at −78° using as short a path length as possible. The exit from the CO_2 trap was connected *via* a manometer to a liquid nitrogen cold-trap and vacuum pump. An air bleed was incorporated into the system and the pressure was maintained at 10 mmHg. Starting from room temperature the contents of the flask were slowly heated using an oil bath. After 2 h the bath temperature was 185° and the reaction was stopped. The liquid collected in the CO_2 trap (16·5 g) was analysed by g.l.c. and shown to contain five components with relative retention times of 1(3%) : 1·6(2%) : 2·7(24%) : 5·0(20%) : 9·7(51%). The components with the shortest and longest

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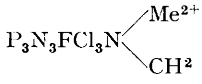
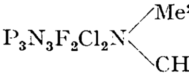
[1] B. Green and D. B. Sowerby, *J. Chem. Soc.* (*A*), 1970, 987.

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

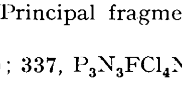
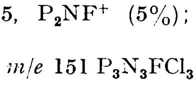
[3] R. Keat and R. A. Shaw, *J. Chem. Soc.*, 1965, 2215.

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

[5] E. Niecke, H. Thamm, and G. Flaskerud, *Chem. Ber.*, 1971, **104**, 3729.

retention times were shown to be $P_3N_3F_4ClNMe_2$ (VII) and unreacted $P_3N_3Cl_5NMe_2$ (I) respectively. Samples of the components with relative retention times of 2·7 and 5·0 were then separated by g.l.c. (5 ft. column containing 15% silicone oil DC 560 at 190°) (Found for the component with the longer retention time: C, 7·6; H, 2·0; N, 16·1. Calc. for $P_3N_3FCl_4NMe_2$: C, 7·1; H, 1·8; N, 16·5%). Evidence from ^{19}F n.m.r. spectroscopy (see later) showed that the sample was a mixture of *cis*- (II) and *trans*- (III) isomers but further attempts to separate these using (i) different stationary phases, *e.g.* diethyleneglycolsuccinate and dinonyl phthalate, (ii) 10 ft. columns and (iii) reduced carrier gas flow rates (down to 15 ml min^{-1}) were unsuccessful. I.r. absorptions of the mixture occurred at 3010w, 2960mw, 2920mw, 2890mw, 2855w, 2815w, 1475mw, 1458m, *ca.* 1440sh, 1293m, *ca.* 1225sh, 1210vs, *ca.* 1190sh, 1147m, 1100vw, 1062m, 1000s, 939m, 897m, 865s, 780s, 711ms, 651ms, 590s, 563s, 525s, 460m, 448m, 430m cm^{-1}. Principal fragment ions: *m/e* 338, $P_3N_3FCl_4NMe_2^+$ (9%); 303, $P_3N_3FCl_3NMe_2^+$ (21%); 295, $P_3N_3FCl_4H^+$ (17%); 294, $P_3N_3FCl_4^+$ (43%); 260, $P_3N_3FCl_3H^+$ (100%); 224, $P_3N_3FCl_2^+$ (42%); 215, $P_2N_2FCl_3H^+$ (5%); 190, $P_3N_3FClH^+$ (8%); 145, $P_2N_2FClH^+$ (10%); 130, P_2NFCl^+ (16%); 95, P_2NF^+ (5%); 85, $PFCl^+$ (9%); 66, PCl^+ (5%). A doubly charged ion *m/e* 151,  $P_3N_3FCl_3N\begin{smallmatrix}\diagup Me^{2+}\\ \diagdown CH^2\end{smallmatrix}$ (10%) was also detected [Found for the component with the shorter retention time (IV): C, 7·5; H, 2·1; N, 16·8. Calc. for $P_3N_3F_2Cl_3NMe_2$: C, 7·4; H, 1·9; N, 17·3%]. I.r. absorptions occurred at: 3010w, 2960mw, 2925mw, 2895mw, 2855w, 2815w, 1475m, 1456m, *ca.* 1440sh, 1290m, 1240vs, 1221vs, 1188sh, 1152m, 1100vw, 1062m, 1003s, 975s, 929s, 918s, 860s, 775w, 758s, 711ms, 625ms, 586s, 530s, 486s, 464m, 433m cm^{-1}. Principal fragment ions: *m/e* 322, $P_3N_3F_2Cl_3NMe_2^+$ (34%); 287, $P_3N_3F_2Cl_2NMe_2^+$ (21%); 279, $P_2N_3F_2Cl_3H^+$ (17%); 278, $P_3N_3F_2Cl_3^+$ (46%); 244, $P_3N_3F_2Cl_2H^+$ (100%); 208, $P_3N_3F_2Cl^+$ (32%); 199, $P_2N_2F_2Cl_2H^+$ (5%); 174, $P_3N_3F_2H^+$ (6%); 129, $P_2N_2F_2H^+$ (6%); 114, $P_2NF_2^+$ (9%); 69, PF_2^+ (7%). A doubly charged ion *m/e* 143,  $P_3N_3F_2Cl_2N\begin{smallmatrix}\diagup Me^{2+}\\ \diagdown CH_2\end{smallmatrix}$ (11%) was also detected. Examination of the petrol-soluble materials remaining in the reaction flask (10·0 g) revealed the presence mainly of starting material together with small amounts of the less fluorinated products.

A second experiment was carried out under the same conditions but with a fractionating column between the reaction flask and the cold trap. The liquid product collected in the cold trap contained three components. Those with the shortest and longest retention times were shown to be $P_3N_3F_4ClNMe_2$ (VII) (68%) and $P_3N_3F_2Cl_3NMe_2$ (IV) (13%) respectively. A sample of the component with the intermediate retention time [which ^{19}F n.m.r. indicated to be a mixture of (V) and (VI)] (19%) was separated by g.l.c. (5 ft. column containing 15% silicone oil DC 560 at 138°) (Found: C, 8·1; H, 2·1; N, 18·2. Calc. for $P_3N_3F_3Cl_2NMe_2$: C, 7·8; H, 2·0; N, 18·2%). This compound was shown by retention times to be identical to the product (relative retention time 1·6) not identified in the previous reaction. I.r. absorptions occurred at: 3010w, 2960m, 2925m, 2900m, 2860w, 2815w, 1480m, 1462m, *ca.* 1450sh, 1300sh, 1250vs, 1200w, 1160m, 1105w, 1068m, 1010m, 988ms, 936s, 908s, 850s, 800vw, 761s, 720ms, 637s, 570s, 550sh, 512ms, 499ms, 475ms, 449sh, 442m cm^{-1}. Principal fragment ions: *m/e* 306, $P_3N_3F_3Cl_2NMe_2^+$ (22%); 271, $P_3N_3F_3ClNMe_2^+$ (22%); 263, $P_3N_3F_3Cl_2H^+$ (10%); 262, $P_3N_3F_3Cl_2^+$ (58%); 228, $P_3N_3F_3ClH^+$ (100%); 227, $P_3N_3F_3Cl^+$ (8%); 192, $P_3N_3F_3^+$ (24%); 183, $P_2N_2F_3ClH^+$ (12%); 148, $P_2N_2F_3H^+$ (5%); 114, $P_2NF_2^+$ (10%); 95, P_2NF^+ (5%); 69, PF_2^+ (11%).

Reaction of Compound (I) *with Antimony Trifluoride.*—A slurry of (I) (5·0 g, 0·014 mol) with SbF_3 (7·5 g, 0·042 mol) and two drops of $SbCl_5$ was slowly heated from room temperature for 3 h. The final oil-bath temperature was 205°. The reaction mixture was worked up as described previously [1] to yield a colourless liquid (1·3 g) which was shown by g.l.c. to contain eleven components with relative retention times of 1(1·5%) : 1·3(1%) : 2·5(10%) : 3·3(6%) : 3·7(1%) : 4·3(1%) : 8·0(10%) : 9·7(trace) : 10·5(trace) : 21·0(68%) : 23·7(1·5%). A sample of the most abundant component (IX) was separated by g.l.c. (5 ft. column containing 15% silicone oil DC 560 at 155°) (Found: C, 7·1; H, 1·9; N, 15·7. $P_3N_3FCl_4NMe_2$ requires: C, 7·1; H, 1·8; N, 16·5%). I.r. absorptions occurred at: 3000w, 2955m, 2925m, 2860mw, 2820w, 1485m, 1460m, 1450sh, 1311m, 1240vs, 1205vs, *ca.* 1160sh, *ca.* 1140sh, 1110vw, 1072m, 1012s, 920m, 900m, 858s, 799ms, 706ms, 639s, 597s, 530s, 478s cm^{-1}. Principal fragment ions: *m/e* 338, $P_3N_3FCl_4NMe_2^+$ (73%); 337,  $P_3N_3FCl_4N\begin{smallmatrix}\diagup Me^{+}\\ \diagdown CH_2\end{smallmatrix}$ (8%); 323, $P_3N_3FCl_4NMe^+$ (19%); 303, $P_3N_3FCl_3NMe_2^+$ (35%); 295, $P_3N_3FCl_4H^+$ (100%); 294, $P_3N_3FCl_4^+$ (49%); 260, $P_3N_3FCl_3H^+$ (88%); 245, $P_3N_2FCl_3^+$ (13%); 224, $P_3N_3FCl_2^+$ (64%); 215, $P_2N_2FCl_3H^+$ (11%); 200, $P_2NFCl_3^+$ (6%); 190, $P_3N_3FClH^+$ (13%); 145, $P_2N_2FClH^+$ (16%); 130, P_2NFCl^+ (21%); 101, PCl_2^+ (7%); 95, P_2NF^+ (5%); 85, $PFCl^+$ (7%). Doubly charged ion: *m/e* 151  $P_3N_3FCl_3N\begin{smallmatrix}\diagup Me^{2+}\\ \diagdown CH_2\end{smallmatrix}$ (23%). A complete investigation of the minor products of the reaction was not possible but a mass spectrum of the product mixture indicated the following parent ions: *m/e* 338, $P_3N_3FCl_4NMe_2^+$ (55%); 331, $P_3N_3F_2Cl_2(NMe_2)_2^+$ (10%); 322, $P_3N_3F_2Cl_3NMe_2^+$ (14%); 313, $P_3N_3F_2Cl_4^+$ (8%); 306, $P_3N_3F_3Cl_2NMe_2^+$ (8%); 299, $P_3N_3F_4(NMe_2)_2^+$ (6%).

Instruments.—A Varian 920 gas chromatograph fitted with stainless steel columns (1/4″ diameter) packed with 60—80 mesh Chromosorb W (AW–HMDS). Helium carrier gas (flow rate *ca.* 75 ml min^{-1}) was used throughout. N.m.r. spectra were recorded for neat liquid samples on a Bruker HFX 5 spectrometer. I.r. spectra were obtained for liquid films in the range 4000—400 cm^{-1} on a Perkin-Elmer 457 spectrometer and mass spectra on an AEI MS 9 spectrometer.

RESULTS

^1H *N.m.r. Spectra.*—The data are summarised in Table 1. Each spectrum consists of one basic doublet arising from the coupling of the protons to the nearest phosphorus atom. The apparent coupling constant, *J**(HP), was measured from the centre of each doublet component which show small second-order splittings due to coupling with fluorine and distant phosphorus atoms. For compounds (II)—(VII) the value of *J**(HP) does not differ markedly from that obtained for $P_3N_3Cl_5NMe_2$ (I), implying that fluorination has taken place on a phosphorus atom not carrying the dimethylamino-group. A value for *J**(HP) of 17—18 Hz

TABLE 1

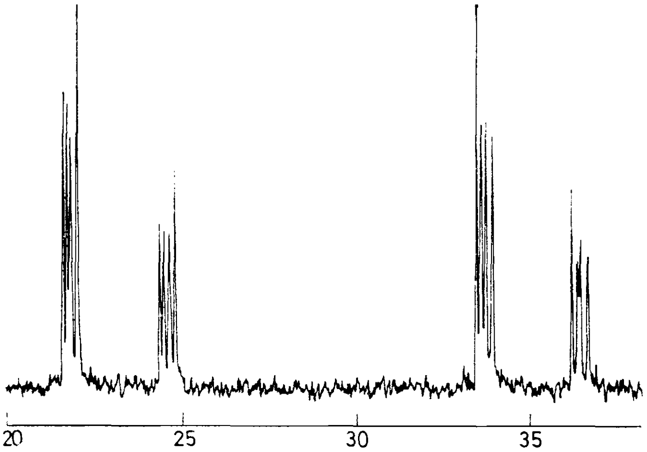
N.m.r. spectra

	Compound	¹H N.m.r. Chemical shift (τ)	¹H N.m.r. J^*(HP)/Hz	¹⁹F N.m.r. Chemical shift [a]	¹⁹F N.m.r. J^*(FP)/Hz
(I)	$P_3N_3Cl_5NMe_2$	7·28	18·0		
(II)	*cis*-$P_3N_3FCl_4NMe_2$	7·28 [b]	17·4	30·5	1010
(III)	*trans*-$P_3N_3FCl_4NMe_2$			27·8	1010
(IV)	$P_3N_3F_2Cl_3NMe_2$	7·29	17·9	68·4	910
				70·7	910
(V)	*cis*-$P_3N_3F_3Cl_2NMe_2$	7·28 [b]	17·0	31·9 (1)	1020
				66·1 [c] (2)	880
(VI)	*trans*-$P_3N_3F_3Cl_2NMe_2$			29·4 (1)	995
				66·1 [c] (2)	880
(VII)	$P_3N_3F_4ClNMe_2$	7·29	17·2	69·8	930
(IX)	$P_3N_3FCl_4NMe_2$	7·25	12·5	63·0	950

[a] P.p.m. upfield from CCl_3F. [b] Separate resonances were not resolved for *cis* and *trans* isomers. [c] PF_2 Resonance of *cis* and *trans* isomers not resolved. Figures in parentheses denote relative intensities.

is typical for compounds containing a $PClNMe_2$ group.[5-7] With the compound $P_3N_3FCl_4NMe_2$ (IX) obtained in the SbF_3 reaction the chemical shift of the dimethylamino-group has moved to lower field and the value of J^*(HP) has dropped to 12·5 Hz. Both these observations are consistent with the presence of a $PFNMe_2$ group.[1,2] A value of J^*(HP) of 12·7 Hz in $P_3N_3F_5NMe_2$ (VIII) has been reported.[4]

¹⁹F *N.M.R. Spectra.*—Data are summarised in Table 1. None of the spectra is first order and detailed analysis has not been carried out but approximate chemical shifts (*ca.* 30 p.p.m. for a PFCl group and *ca.* 70 p.p.m. for PF_2) and coupling constants [J^*(FP)] [8,9] obtained directly from the spectra can be used to characterise unambiguously the compounds.



¹⁹F N.m.r. spectrum of a mixture of *cis*-(II) and *trans*-(III) $P_3N_3FCl_4NMe_2$

The spectrum of the monofluoride, $P_3N_3FCl_4NMe_2$, obtained by the KSO_2F reaction, is reproduced in the Figure and bears a marked similarity to that for $P_3N_3FCl_5$.[10] The presence of *cis*- and *trans*-isomers shows clearly and by the previously noted trend,[1,2] in which a fluorine atom on the same side of the ring as the dimethylamino-group is more shielded than one on the opposite side to a dimethylamino-group, the low field resonance is assigned to the *trans*-isomer (III) and the high field resonance to the *cis*-isomer (II). Integration of the spectrum gives a *cis* : *trans* ratio of 1 : 2·3. It was not possible to separate pure samples of the *cis*- and *trans*-isomer by g.l.c. as noted in the Experimental section.

The spectrum of the difluoride, $P_3N_3F_2Cl_3NMe_2$ (IV) indicates the presence of a PF_2 group. The chemical shifts were obtained by considering the chemically non-equivalent fluorine atoms, F_A and F_B, as the AB part of an ABX spin system. The high field resonance is assigned to F_B which is on the same side of the ring as the amine group.

The spectrum of the trifluoride, $P_3N_3F_3Cl_2NMe_2$, again confirms a geminal arrangement of fluorine atoms and the presence of *cis*- (V) and *trans*- (VI) isomers. Two resonances (of combined intensity one), each split by coupling to phosphorus, at 31·9 and 29·4 p.p.m. are assigned to F_C and F_D in structures (V) and (VI) respectively. A broad doublet of intensity two at 66·1 p.p.m., which does not however show splitting due to the two isomers confirms the presence of a PF_2 group. Integration of the PFCl resonances gives the *cis* : *trans* ratio as 1 : 1·2.

For $P_3N_3F_4ClNMe_2$ (VII) a very complex spectrum is obtained but the apparent chemical shift indicates the presence of PF_2 groups only, which confirms a geminal structure.

The spectrum of the monofluoride (IX), obtained by the SbF_3 reaction, consists of one resonance split into a widely spaced doublet [J^*(FP)]. Each component shows further smaller second order splittings. The chemical shift (63·0 p.p.m.) compares well with the value found for $PFNMe_2$ groups in other dimethylaminofluorocyclotriphosphazenes.[1,2,4,5]

Infrared Spectra.—The assignment of the i.r. spectra closely follows that for bis-, tris-, and tetrakis-dimethylamino-derivatives [2] with amine and ring vibrations occurring in the expected positions. Structural information is most readily obtained from phosphorus–chlorine and phosphorus–fluorine stretching vibrations summarised in Table 2 and these will be discussed in detail. Where two frequencies are given for a particular vibration these are assigned to in-phase and out-of-phase components. In the absence of reliable polarisation measurements in the Raman, a complete assignment cannot be made.

(a) *Phosphorus–chlorine vibrations.* The tetrafluoride $P_3N_3F_4ClNMe_2$ (VII) shows a single intense band at 588 cm⁻¹ in a region transparent in $P_3N_3F_5NMe_2$ [4,5] and is thus

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[6] C. T. Ford, F. E. Dickson, and I. I. Bezman, *Inorg. Chem.*, 1964, **3**, 177.

[7] R. Keat and R. A. Shaw, *J. Chem. Soc.* (*A*), 1968, 703.

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

[9] P. Clare, D. B. Sowerby, and B. Green, *J.C.S. Dalton*, 1972, 2374.

[10] F. Heatley and S. M. Todd, *J. Chem. Soc.* (*A*), 1966, 1152.

assigned to νPCl. The two vibrations expected for $P_3N_3F_3Cl_2NMe_2$ are similarly assigned at 637 and 570 cm^{-1}. With $P_3N_3F_2Cl_3NMe_2$ (IV) strong bands occur at 625, 586, and 530 cm^{-1}. Although a band as high as 637 cm^{-1} in $P_3N_3F_3Cl_2NMe_2$ can be assigned to νPCl it is better here to assign νPCl to the band at 586 cm^{-1}, close to the value found for this vibration in the tetrafluoride (VII), leaving bands at 625 and 530 cm^{-1} to be assigned to $\nu_{as}PCl_2$ and ν_sPCl_2 respectively. Similarly the four bands predicted for $P_3N_3FCl_4NMe_2$ (KSO_2F reaction) occur at 651 ($\nu_{as}PCl_2$), 590 and 563 (νPCl), and 525 cm^{-1} (ν_sPCl_2). In contrast, of the four vibrations expected for the isomeric monofluoride (IX) produced in the SbF_3 reaction, one (ν_sPCl_2 i.p.) has been assigned [11] below the region covered in this work and thus only three absorptions are observed in this region. It should also be mentioned that the spectrum [12] of $P_3N_3Cl_5NMe_2$ (I) is deceptively simple in this region. Bands at 650 and 540 cm^{-1} can be assigned to $\nu_{as}PCl_2$ and ν_sPCl_2 respectively leaving only one band at 588 cm^{-1} arising from the accidental degeneracy of νPCl and the second component of $\nu_{as}PCl_2$.

TABLE 2

Phosphorus–fluorine and phosphorus–chlorine stretching vibrations/cm^{-1}

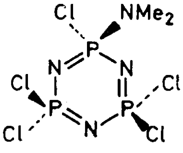
Compound	$\nu_{as}PCl_2$	ν_sPCl_2	νPCl	$\nu_{as}PF_2$	ν_sPF_2	νPF
$P_3N_3Cl_5NMe_2$	650, 588	540	588			
$P_3N_3FCl_4NMe_2$ (SbF_3 reaction)	639, 597	530				858
$P_3N_3FCl_4NMe_2$ (KSO_2F reaction)	651	525	590, 563			865
$P_3N_3F_2Cl_3NMe_2$	625	530	586	975	758	
$P_3N_3F_3Cl_2NMe_2$			637, 570	988	761	850
$P_3N_3F_4ClNMe_2$			588	1018, 980	834 752	

(b) *Phosphorus–fluorine stretching vibrations*. The assignment of νPF to a strong band at 858 cm^{-1} in $P_3N_3FCl_4NMe_2$ (IX) and at 865 cm^{-1} in the corresponding isomers (II and III) from the KSO_2F reaction is strongly supported as this region is transparent in $P_3N_3Cl_5NMe_2$. The difluoride, $P_3N_3F_2Cl_3NMe_2$ (IV) shows sharp bands at 975 ($\nu_{as}PF_2$) and 758 cm^{-1} (ν_sPF_2) close to the values found in the 1,3-bisdimethylamino-5,5-difluoro-isomers of $P_3N_3F_2Cl_2(NMe_2)_2$ [1] while the trifluoride, $P_3N_3F_3Cl_2NMe_2$ possesses, in addition to bands at 988 ($\nu_{as}PF_2$) and 761 cm^{-1} (ν_sPF_2), a single intense absorption at 850 cm^{-1} (νPF). $P_3N_3F_4ClNMe_2$ (VII) is the only compound to possess two absorptions at *ca.* 1000 cm^{-1} (in addition to ν_sNC_2) and so vibrations at 1018 and 980 cm^{-1} can be assigned to $\nu_{as}PF_2$. Vibrations arising from ν_sPF_2 modes are assigned at 752 cm^{-1} (in-phase) and 834 cm^{-1} (out-of-phase) following Emsley's [11] assignments for the geminal chlorofluorocyclotriphosphazenes.

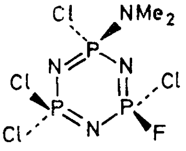
Mass Spectra.—For all the compounds considered parent ions with the appropriate chlorine isotope patterns are observed. A significant difference is noted in the intensity of the parent ion in the isomeric monofluorides, $P_3N_3FCl_4NMe_2$. In the molecule containing the $PFNMe_2$ group (IX) the intensity is 73% (relative to the base peak) whilst in the compound from the KSO_2F reaction the intensity is only 9%. As expected loss of chlorine together with a much weaker loss of fluorine is a common feature but in contrast to $P_3N_3Cl_6$ [13] and the non-geminal series $P_3N_3F_nCl_{6-n}$ (n = 2—4) [12] the base peak in no case arises from the loss of a chlorine atom. For the monofluoride from the SbF_3 reaction (IX) the base peak, $P_3N_3FCl_4H^+$ arises from the loss of 43 mass units (possibly ethylenimine, or $CH_3-N=CH_2$). Such hydrogen containing species and metastable ions corresponding to the loss of 43 mass units are a common feature of the fragmentation of dimethylaminocyclophosphazenes.[14] Protonic species have also been observed during the fragmentation of *NN'*-dimethylenediaminecyclophosphazenes.[15] In contrast, the base peak for the series $P_3N_3F_nCl_{5-n}NMe_2$ (n = 1—4) produced in the KSO_2F reaction, can be considered to arise by the loss of a chlorine atom plus 43 mass units from the parent ion. These differences may be of use in future structural determinations.

DISCUSSION

In contrast to cyclotriphosphazenes carrying two or more dimethylamino-groups which do not react with sodium fluoride,[1,2] the monodimethylamino-derivative, $P_3N_3Cl_5NMe_2$ reacts to form a tetrafluoride, $P_3N_3F_4ClNMe_2$ (VII). As expected the presence of the amine group directs attack to the PCl_2 groups but the formation of some of the fully fluorinated compound $P_3N_3F_5NMe_2$ (VIII) implies that the total electron density on the phosphorus atom of the $PClNMe_2$ is not too great to prevent further attack here. Indeed with fluorosulphite which is a stronger nucleophile than F$^-$, the major product is the pentafluoride $P_3N_3F_5NMe_2$ (VIII) together with a small amount of the geminal tetrafluoride (VII).



(I)



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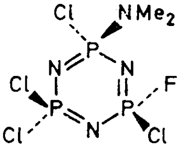

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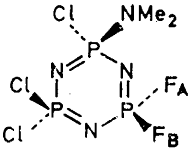

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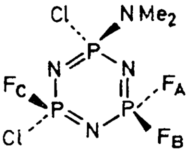

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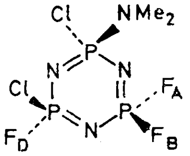
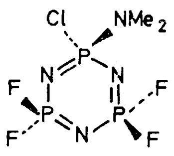
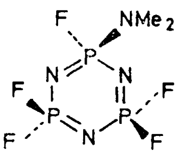


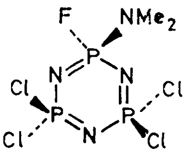
(VI)



(VII)



(VIII)



(IX)

There are difficulties associated with the separation of

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[11] J. Emsley, *J. Chem. Soc.* (*A*), 1970, 109.

[12] B. Green, Ph.D. Thesis, Nottingham University, 1970.

[13] C. E. Brion and N. L. Paddock, *J. Chem. Soc.* (*A*), 1968, 388.

[14] B. Green, to be published.

[15] T. Chivers and R. Hedgeland, *Canad. J. Chem.*, 1972, **50**, 1017.

these volatile higher fluorides from the solvent and so a reaction in the absence of solvent was attempted to facilitate product separation. Furthermore, it is difficult to prepare the lesser fluorinated derivatives in solution because the introduction of fluorine increases the susceptibility of the molecule towards nucleophilic attack.[8] By removing the product *in vacuo* as soon as it is formed it was possible to obtain the series $P_3N_3F_nCl_{5-n}NMe_2$ (n = 1—4). The replacement scheme is geminal with attack occurring at the PCl_2 groups. No pentafluoride was detected in this reaction. It is only for compounds when n = 1 and 3 that *cis* and *trans* isomers are possible and in each case both isomers are formed but it was not possible to separate them by g.l.c.

More interesting is the reaction with antimony trifluoride which has been shown [1,2] to be a preferential fluorinating agent for $PClNMe_2$ groups. Fluorination of tris- and tetrakis-dimethylaminochlorocyclophosphazenes takes place in 1,2-dichloroethane [2] but with the bisdimethylamino-compound, $P_3N_3Cl_4(NMe_2)_2$ it is necessary to carry out the reaction in refluxing *sym*-tetrachloroethane.[1] For the less basic mono-derivative, $P_3N_3Cl_5NMe_2$, no reaction occurs in *sym*-tetrachloroethane but at higher temperatures and in the absence of a solvent reaction does occur slowly. It is better if the reaction is carried out in the presence of a catalytic quantity of $SbCl_5$ which forms SbF_3Cl_2 [16] as the active fluorinating species. This is likely to be a stronger Lewis acid than SbF_3 and so is able to co-ordinate to the weak base, $P_3N_3Cl_5NMe_2$ as a means of reaction and giving as the major product (68%) a monofluoride, $P_3N_3FCl_4NMe_2$ (IX) in which the fluorine atom is attached to the amine substituted phosphorus atom. Ten other components were detected in the reaction mixture and mass spectrometry showed the presence of (a) more highly fluorinated species of the type $P_3N_3F_nCl_{5-n}NMe_2$ (n = 2 and 3), (b) species containing two dimethylamino-groups [$P_3N_3F_3Cl_2(NMe_2)_2$ and $P_3N_3F_4(NMe_2)_2$] and (c) one species, $P_3N_3F_4Cl_2$, containing no amine groups. The replacement of dimethylamino-groups by SbF_3 has been demonstrated [17] for both $P_3N_3(NMe_2)_6$ and $P_4N_4(NMe_2)_8$ and so compounds belonging to the series $P_3N_3F_nCl_{6-n}$ are to be expected. The formation of bisdimethylamino-derivatives can be rationalised by forming an antimony–amine species on deaminolysis of $P_3N_3Cl_5NMe_2$ which then aminates $P_3N_3Cl_5NMe_2$. However none of the rearrangement products constitute more than 10% of the reaction product and the major product is again one in which the $PClNMe_2$ group has been selectively fluorinated.

[3/1861 *Received, 7th September, 1973*]

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[16] A. L. Henne, *Org. Reactions*, **1944**, **2**, 49.

[17] P. Clare, D. Millington, and D. B. Sowerby, *J.C.S. Chem. Comm.*, 1972, 324.