343. *Phosphonitrilic Derivatives. Part V.*[1] *The Triphosphonitrilic Fluoride Chlorides.*

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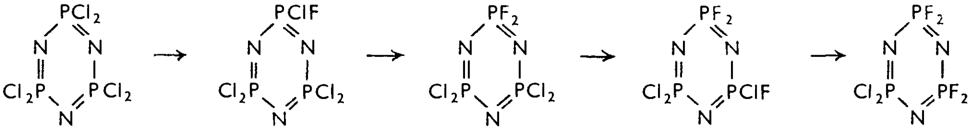
Triphosphonitrilic trifluoride trichloride, $P_3N_3F_3Cl_3$, and new isomers of triphosphonitrilic difluoride tetrachloride, $P_3N_3F_2Cl_4$, and triphosphonitrilic tetrafluoride dichloride, $P_3N_3F_4Cl_2$, have been isolated from the products of partial fluorination of triphosphonitrilic chloride. The infrared and nuclear magnetic resonance spectra of these compounds and of the previously reported isomer of the tetrafluoride dichloride enable assignments of their structures to be made. These structures and the relative yields of the compounds show that a PFCl group is more easily fluorinated than a PCl_2 group.

THE reaction of potassium fluorosulphite with the cyclic phosphonitrilic chlorides has previously been used to prepare the corresponding phosphonitrilic fluorides.[2,3] Some trimeric phosphonitrilic fluoride chlorides have now been prepared by allowing only partial reaction between triphosphonitrilic chloride and potassium fluorosulphite. The previously reported tetrafluoride dichloride[4] is shown to be triphosphonitrilic 1,1,3,3-tetrafluoride 5,5-dichloride, and the new compounds triphosphonitrilic 1,1-difluoride 3,3,5,5-tetrachloride, 1,1,3-trifluoride 3,5,5-trichloride, and 1,1,3,5-tetrafluoride 3,5-dichloride have been isolated. The following sequence for the main substitutions is suggested.



This sequence is supported by the high yields of the tetrafluoride dichloride relative to that of the trifluoride trichloride, and of the difluoride tetrachloride relative to that of the absent monofluoride pentachloride, both showing that a PFCl group is more easily fluorinated than a PCl_2 group. Further support comes from the absence of the 1,3,5-trifluoride 1,3,5-trichloride and the small amount of 1,1,3,5-tetrafluoride 3,5-dichloride formed, although some of this low-boiling isomer may have evaporated during storage.

The preferential fluorination of a PFCl group would be expected on the simple basis that the susceptibility of the phosphorus atom to nucleophilic attack should be increased by a single substituent of higher electronegativity than chlorine. It is interesting to contrast these results with those obtained in work on the replacement of the chlorine atoms by amine groups,[5] where successive replacement normally occurs at different phosphorus atoms. This may be partly due to steric hindrance, but in view of the known tendency of phosphorus and other second-row elements to accept electrons from neighbouring atoms,[6] it is probable that a second replacement at the same phosphorus atom in these cases is also hindered by the partial feed-back of " lone-pair " electrons from nitrogen atoms in the substituent groups.

EXPERIMENTAL

Materials.—Potassium fluorosulphite was prepared by shaking anhydrous potassium fluoride with liquid sulphur dioxide in an autoclave for 12—16 days. The increase in weight of the

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[1] Part IV, Hartley, Paddock, and Searle, *J.*, 1961, 430.
[2] Seel and Langer, *Angew. Chem.*, 1956, **68**, 461.
[3] Part III, Chapman, Paddock, Paine, Searle, and Smith, *J.*, 1960, 3608.
[4] Schmitz-Dumont and Braschos, *Z. anorg. Chem.*, 1939, **243**, 113.
[5] Becke-Goehring and John, *Angew. Chem.*, 1957, **70**, 657; Ray and Shaw, *Chem. and Ind.*, 1959, 53; Becke-Goehring, John, and Fluck, *Z. anorg. Chem.*, 1959, **302**, 103.
[6] Henbest, *Ann. Reports*, 1956, **53**, 137.

solid indicated the composition KF : SO_2 = 1 : 0·5—0·6. Other materials have been described previously.[3]

Preparation of Phosphonitrilic Fluoride Chlorides.—In one experiment, an intimate mixture of potassium fluorosulphite and triphosphonitrilic chloride was heated at 120—140°. After removal of dissolved sulphur dioxide, the volatile products were distilled to yield a colourless liquid mixture of fluoride chlorides. In the second preparation, a mixture of triphosphonitrilic chloride and anhydrous potassium fluoride was heated with sulphur dioxide in a rocking autoclave at 110° for 7½ days. Volatile products were distilled off *in vacuo* and fractionated into triphosphonitrilic fluoride and a colourless liquid mixture of fluoride chlorides. This was combined with the product from the first experiment and again fractionated (reflux ratio greater than 30). The fractions were combined into five groups on the basis of their infrared spectra (CS_2 solution; Perkin–Elmer model 21 spectrometer).

Characterisation of Triphosphonitrilic Fluoride Chlorides.—The following fractions were identified: (1) 1,1,3,5-tetrafluoride 3,5-dichloride (0·5 g.), b. p. 84·4° ± 0·2°, ν (P=N) 1283, 1276; (2) 1,1,3,3-tetrafluoride 5,5-dichloride (21·6 g.), b. p. 114·7° ± 0·2° (lit.,[4] 115—117°), ν (P=N) 1277, 1253; (3) 1,1,3-trifluoride 3,5,5-trichloride (1·5 g.), b. p. 150·1° ± 0·2°, ν (P=N) 1258, 1237; and (4) 1,1-difluoride 3,3,5,5-tetrachloride (5·8 g.), b. p. 181·6° ± 0·2°, ν (P=N) 1246, 1226. Analyses are tabulated. Identifications are described below. Previous values [3,7] of ν (P=N) are 1297 cm.$^{-1}$ for $(PNF_2)_3$ and 1218 cm.$^{-1}$ for $(PNCl_2)_3$.

	Found (%, except *M*)						Reqd. (%, except *M*)				
Fraction	P	N	F	Cl	*M*	Formula	P	N	F	Cl	*M*
1	—	—	26·6	—	—	$P_3N_3Cl_2F_4$	—	—	27·0	—	—
2	32·9	14·7	26·1	24·5	290	$P_3N_3Cl_2F_4$	33·0	14·9	27·0	25·2	282
3	—	13·8	19·1	35·7	307	$P_3N_3Cl_3F_3$	—	14·1	19·1	35·7	298
4	29·3	13·0	11·9	43·8	314	$P_3N_3Cl_4F_2$	29·5	13·3	12·1	45·1	315

The frequencies of the P=N stretching vibration follow a smooth trend with increasing fluorine substitution, and confirm that all the fractions are trimeric; if they were tetrameric the P=N frequencies would be expected to fall between those of the tetrameric chloride [7] (1315 cm.$^{-1}$) and the tetrameric fluoride [3] (1428 cm.$^{-1}$).

Vapour-phase chromatography showed that the purity of the separated compounds was approximately 89%, 94%, 97%, and 97% respectively for the four fractions. This technique also showed the presence of another compound, besides triphosphonitrilic chloride, in the distillation residue, but this compound could not be isolated in characterisable quantities. Minute quantities of several other compounds were also present in the various fractions.

Nuclear magnetic resonance spectra of the three main fractions were obtained with a Varian V4300B high-resolution spectrometer, operating at 12 Mc./sec. for phosphorus and at 40 and 12 Mc./sec. for fluorine. Specimens were contained in sealed tubes of outside diameter either 12 or 5 mm. The spectra show a great deal of fine structure, which was not always fully resolved. The main features of the spectra, however, provide sufficient structural information. An analysis of the spectrum of triphosphonitrilic difluoride tetrachloride will be published separately.

Structures of the Triphosphonitrilic Fluoride Chlorides.—(a) *Triphosphonitrilic* 1,1,3,3-*tetrafluoride* 5,5-*dichloride and* 1,1,3,5-*tetrafluoride* 3,5-*dichloride.* On the basis of the data in the Table, fraction 2 may be identified with the previously reported triphosphonitrilic tetrafluoride dichloride;[4] fraction 1 is a new isomer, *triphosphonitrilic* 1,1,3,5-*tetrafluoride* 3,5-*dichloride.*

For triphosphonitrilic tetrafluoride dichloride there may be three isomers, 1,1,3,3-, *cis*-1,1,3,5-, and *trans*-1,1,3,5-. Since triphosphonitrilic chloride [7] and fluoride [8] have D_{3h} symmetry, these fluoride chloride isomers probably have C_{2v}, C_s, and C_2 symmetry respectively. The degeneracy of the P=N ring stretching vibration [3] would be resolved in all the isomers. Since the deviation from three-fold symmetry in the 1,1,3,3-isomer (C_{2v}) is roughly twice that in the others, the splitting of the degenerate vibration should be much larger in the 1,1,3,3-isomer than in the other two isomers, in which the splittings would be about equal. On this basis, therefore, the high-boiling isomer (fraction 2) of the tetrafluoride dichloride (splitting 24 cm.$^{-1}$) may be identified with the 1,1,3,3-isomer (C_{2v}), and the low-boiling isomer (fraction 1) (splitting 7 cm.$^{-1}$) with one of the 1,1,3,5-isomers (C_s or C_2).

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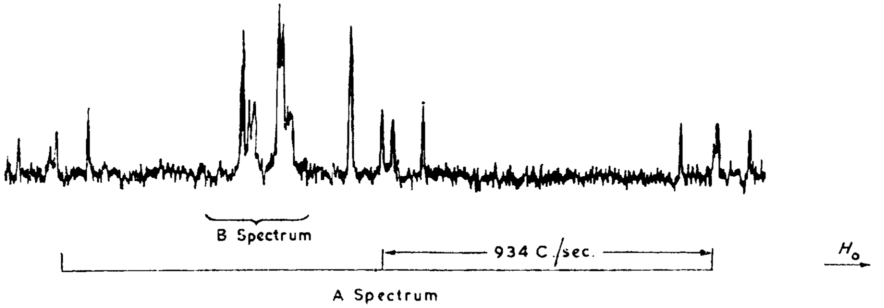
[7] Daasch, *J. Amer. Chem. Soc.*, 1954, **76**, 3403.
[8] Chapman, unpublished work.

The fluorine nuclear magnetic resonance spectrum of fraction 2 consists of two peaks, each showing fine structure, with a separation of about 860 c./sec. at both 12 and 40 Mc./sec. This spectrum must be due to a single fluorine species, spin–spin coupled with phosphorus, showing that the compound must be the 1,1,3,3-tetrafluoride 5,5-dichloride. The phosphorus spectrum confirms this, being of the type [9] AB_2 with the B spectrum split into a triplet of separation 860 c./sec.

(b) *Triphosphonitrilic* 1,1-*difluoride* 3,3,5,5-*tetrachloride*. Fraction 4 may be identified as this compound, but the discrepancy between the present b. p. and that previously reported [4] suggests that the present compound is a different isomer. There are three possible isomers, having similar substitution types and symmetries to those of the tetrafluoride dichloride. Since fraction 4 has a splitting (20 cm.$^{-1}$) comparable with that of the 1,1,3,3-tetrafluoride 5,5-dichloride, this product may be identified with the 1,1-*difluoride* 3,3,5,5-*tetrachloride*.

Phosphorus nuclear magnetic resonance spectrum of triphosphonitrilic 1,1-*difluoride* 3,3,5,5,-*tetrachloride.*



The phosphorus nuclear magnetic resonance spectrum, shown in the Figure, is basically of the type AB_2, the phosphorus spin–spin coupling being comparable with the chemical shift between the two phosphorus species. The A spectrum is split into a triplet with a separation of 934 c./sec. This spectrum therefore confirms the 1,1-difluoride tetrachloride structure; the alternative 1,3-difluoride 1,3,5,5-tetrachloride structure would give a doublet splitting of the B spectrum of 934 c./sec. and no first-order A splitting.

The fluorine spectrum, both at 40 and at 12 Mc./sec., consists of two peaks separated by 934 c./sec. each showing fine structure. There is no indication of non-equivalence of fluorine atoms due to non-planarity of the ring.

The discrepancy between the b.p. of triphosphonitrilic 1,1-difluoride 3,3,5,5-tetrachloride and that previously reported for this compound [4] suggests that the earlier compound was not the 1,1-difluoride. This is most surprising, since the previously reported difluoride tetrachloride was obtained with the 1,1,3,3-tetrafluoride 5,5-dichloride from a high polymer of tetraphosphonitrilic tetrafluoride tetrachloride.[4] However, the suggestion is supported empirically by the fact that the b. p.s of triphosphonitrilic fluoride (51°), the 1,1,3,3-tetrafluoride 5,5-dichloride (114·7°), the 1,1,3-trifluoride 3,5,5-trichloride (150·1°), the 1,1-difluoride 3,3,5,5-tetrachloride (181·6°) and the chloride (256°) all lie on a smooth curve when plotted against the degree of substitution, while the value reported previously for the difluoride tetrachloride lies below the curve, in much the same way as the value for the 1,1,3,5-tetrafluoride 3,5-dichloride does.

(c) *Triphosphonitrilic* 1,1,3-*trifluoride* 3,5,5-*trichloride*. Fraction 3 may be identified as this *compound*. There are three possible isomers, 1,1,3-, *cis*-1,3,5-, and *trans*-1,3,5-, of probable symmetry C_1, C_{3v}, and C_s respectively. The splitting of the degenerate P=N vibration should be absent in the *cis*-1,3,5-isomer (C_{3v}), very small in the *trans*-1,3,5-isomer, and comparable with the splittings for the 1,1,3,3-tetrafluoride 5,5-dichloride and the 1,1-difluoride 3,3,5,5-tetrachloride in the 1,1,3-trifluoride. In fact the splitting (21 cm.$^{-1}$) is very similar to those for the 1,1,3,3-tetrafluoride 5,5-dichloride and the 1,1-difluoride 3,3,5,5-tetrachloride, and the trichloride may therefore be identified with the 1,1,3-isomer (C_1). This structure is also consistent with the formation of the trifluoride trichloride by fluorination of the 1,1-difluoride tetrachloride.

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[9] Pople, Schneider, and Bernstein, " High Resolution Nuclear Magnetic Resonance," McGraw-Hill, New York, 1959, p. 123.

The fluorine spectrum consists of two doublets, of relative areas ~2 : 1, having field independent separations of 880 and 1000 c./sec., respectively, for the stronger and the weaker doublet. The separation between the centres of the two doublets is 460 c./sec. at 12 Mc./sec. and 1600 c./sec. at 40 Mc./sec. The molecule therefore contains two fluorine species in relative amounts 2 : 1, each fluorine atom being spin–spin coupled to a phosphorus atom. This spectrum is therefore consistent with either the 1,1,3- or the *trans*-1,3,5-trifluoride.

The phosphorus spectrum of the *trans*-1,3,5-isomer would be of type AB_2, with both the A and B spectra split into doublets by phosphorus–fluorine coupling. Since the phosphorus atoms would be chemically equivalent, the chemical shift between the phosphorus species, arising only from the non-equivalence of the fluorine atoms, would be very small; the spectrum would therefore consist of two groups of lines separated by about 1000 c./sec. The phosphorus spectrum of the 1,1,3-isomer, on the other hand, would be of type ABC, with the A spectrum split into a triplet and the B into a doublet by spin–spin interaction with the fluorine nuclei. The spectrum would contain many lines spread over a range of about 2000 c./sec. The observed phosphorus spectrum is in agreement with this, extending over nearly 2000 c./sec., with a singlet/doublet/triplet structure just discernible, confirming that the compound is the 1,1,3-isomer.

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