Fluorination of Aminochlorotriphosphonitriles and the Preparation of Non-geminal Chlorofluorotriphosphonitriles

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Summary Fluorination of dimethylaminochlorotriphosphonitriles with antimony trifluoride and potassium fluorosulphite follows different paths; amino-fluorides from the antimony trifluoride reaction can be converted by hydrogen chloride into non-geminally substituted chlorofluorotriphosphonitriles.

FLUORINATION of $P_3N_3Cl_6$ provides a clear example of an exclusively geminal substitution path,[1] but mixtures of all possible geminal substitution products usually result. Recently, pure $P_3N_3ClF_5$ has been synthesized,[2] and we now report the directed synthesis of two further chloride fluorides, the non-geminally substituted isomer of $P_3N_3Cl_4F_2$ and $P_3N_3Cl_3F_3$.

When 1,3-bisdimethylaminotetrachlorotriphosphonitrile was fluorinated with antimony trifluoride, replacement of the chlorine atoms at the amine-substituted phosphorus atoms occurred. The resulting mixture of *cis-* and *trans-* $P_3N_3Cl_2F_2(NMe_2)_2$ isomers can then be separated by g.l.c. With potassium fluorosulphite, KSO_2F, preferential fluorination occurred at the PCl_2 group and a further pair of *cis-* and *trans*-$P_3N_3Cl_2F_2(NMe_2)_2$ isomers resulted. The four isomers can be differentiated by their retention times, i.r. spectra, and n.m.r. spectra. A non-geminally substituted $P_3N_3Cl_4F_2$ has been prepared by treating the mixture of $P_3N_3Cl_2F_2(NMe_2)_2$ isomers obtained by the antimony trifluoride reaction in nitrobenzene with hydrogen chloride. The product, purified by g.l.c., boils at 170°, compared with 182° for the 1,1-difluoride.[1] The stoicheiometry was confirmed by mass spectrometry and an i.r. spectrum markedly different from that reported for the geminal isomer confirms the preparation of the 1,3-isomer.

Similarly, fluorination of *trans*-1,3,5-trisdimethylaminotrichlorotriphosphonitrile with antimony trifluoride gave the non-geminal amino-fluoride which was converted into 1,3,5-trifluorotrichlorotriphosphonitrile by hydrogen chloride. G.l.c. indicated the presence of one isomer and mass spectrometry confirmed the stoicheiometry as $P_3N_3Cl_3F_3$. The product boils at 140° compared with 150° for the 1,1,3-(geminal) isomer,[1] and the two isomers have markedly different i.r. spectra.[1,3]

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[1] J. Emsley and N. L. Paddock, *J. Chem. Soc.* (*A*), 1968, 2590; A. C. Chapman, D. H. Paine, H. T. Searle, D. R. Smith, and R. F. M. White, *J. Chem. Soc.*, 1961, 1768.

[2] O. Glemser, E. Niecke, and H. W. Roesky, *Chem. Comm.*, 1969, 282.

[3] A. C. Chapman and N. L. Paddock, *J. Chem. Soc.*, 1962, 635.