

Alkylaminopentafluorophosphazenes¹

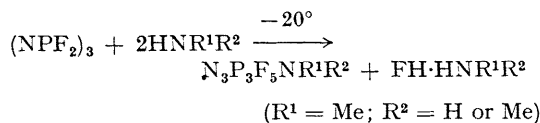
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Summary Alkylaminopentafluorotriphosphazenes have been obtained in good yield by reaction of hexafluorotriphosphazene and alkylamines; they react with hydrogen halides to give halogenopentafluorotriphosphazenes.

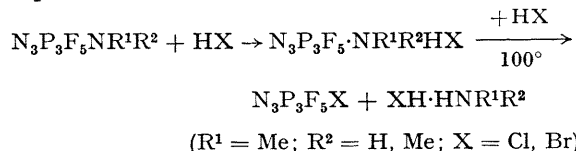
HEXACHLOROTRIPHOSPHAZENE reacts with primary and secondary amines to give alkyl(aryl)aminochlorotriphosphazenes.² Corresponding substitution products of trimeric phosphonitrilic fluoride have not previously been reported.

We have synthesized methyl- (I) and dimethyl-amino-pentafluorotriphosphazenes (II) in good yield by reaction of (NPF₂)₃ and H₂NMe or HNMe₂ in ether:



At room temperature, the amines are stable, colourless liquids, b.p. 151° (I), 140° (II).

In a controlled reaction with hydrogen halides the amines give the corresponding monohalogeno-substitution products through the intermediate quaternary aminopentafluorotriphosphazenes:



Chloro- (III) and bromo-pentafluorotriphosphazenes (IV) are

colourless liquids, fuming in moist air; b.p.: 81° (III), 97° (IV). Up to now they have only been prepared by uncontrolled fluorination of (NPCI₂)₃³ and (NPBr₂)₃.⁴ The compounds reported have been characterized by chemical analysis, molecular-weight determination, and mass spectra. All compounds show the molecular ion as the second strongest peak. In the i.r. spectra the strongest absorption bands, corresponding to the asymmetric (P-N-P) vibrations are observed at: 1262 (I), 1268 (II), 1276 and 1270 (III), and 1276 and 1264 cm.⁻¹ (IV). The fluorine n.m.r. spectra show two pairs of complex multiplets centred at the following frequencies (p.p.m. relative to external CFCI₃):

Compound	δ ¹⁹ F(FP)	δ ¹⁹ F(F ₂ P)
(I)	62.5	70.7
(II)	63.0	70.9
(III)	32.0	71.2
(IV)	20.5	70.8

The proton shifts in the amines (relative to Me₄Si) are:

Compound	δ ¹ H(CH ₃)	δ ¹ H(NH)
(I)	-2.75	-3.70
(II)	-2.78	—

Reaction of hexafluorotriphosphazene with methylamine and dimethylamine under vigorous conditions yield substitution products P₃N₃(NR¹R²)_nF_{6-n} with n > 1. Stronger nucleophiles such as HNEt₂ lead to cleavage of the P-N ring system.

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¹ Previous paper in this series: E. Niecke, O. Glemser, and H. W. Roesky, *Angew. Chem.*, in the press.

² R. A. Shaw, *Rec. Chem. Progr.*, 1967, **28**, 243.

³ A. C. Chapman, D. H. Paine, H. T. Searle, D. R. Smith, and R. F. White, *J. Chem. Soc.*, 1961, 1768; see also, J. Emsley and N. L. Paddock, *J. Chem. Soc. (A)*, 1968, 2590.

⁴ E. Steger and D. Klemm, *J. Inorg. Nuclear Chem.*, 1967, **29**, 1812.