Alkylaminopentafluorophosphazines[1]

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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-aminopentafluorotriphosphazenes (II) in good yield by reaction of $(NPF_2)_3$ and H_2NMe or $HNMe_2$ in ether:

$$(NPF_2)_3 + 2HNR^1R^2 \xrightarrow{-20^\circ} N_3P_3F_5NR^1R^2 + FH\cdot HNR^1R^2$$

$$(R^1 = Me;\ R^2 = H \text{ or } Me)$$

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:

$$N_3P_3F_5NR^1R^2 + HX \rightarrow N_3P_3F_5\cdot NR^1R^2HX \xrightarrow[100^\circ]{+HX} N_3P_3F_5X + XH\cdot HNR^1R^2$$

$$(R^1 = Me;\ R^2 = H, Me;\ X = Cl, Br)$$

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 $(NPCl_2)_3$[3] and $(NPBr_2)_3$.[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 $CFCl_3$):

Compound	$\delta^{19}F(FP)$	$\delta^{19}F(F_2P)$
(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 Me_4Si) are:

Compound	$\delta^1H(CH_3)$	$\delta^1H(NH)$
(I)	−2·75	−3·70
(II)	−2·78	—

Reaction of hexafluorotriphosphazene with methylamine and dimethylamine under vigorous conditions yield substitution products $P_3N_3(NR^1R^2)_nF_{6-n}$ with $n > 1$. Stronger nucleophiles such as $HNEt_2$ lead to cleavage of the P–N ring system.

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