

LITERATURE CITED

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REACTION OF PERFLUOROISOBUTYLENE AND PERFLUOROPROPYLENE
WITH N-TRIMETHYLSILYLPHOSPHAZENES

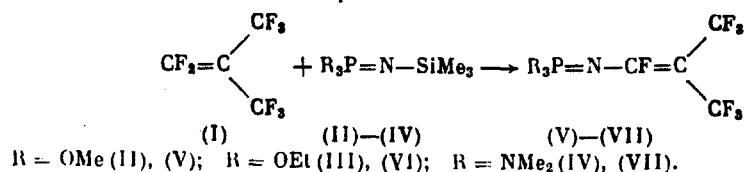
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Perfluoroisobutylene and perfluoropropylene react with N-trimethylsilylphosphazenes to give perfluoroalkenylphosphazenes $R_3P=N-CF=CX-CF_3$ ($R = AlkO, NR_2^1, X = F, CF_3$). The corresponding dialkyl fluorophosphates $(AlkO)_2P(O)F$, were obtained upon the pyrolysis of the alkoxyphosphazenes.

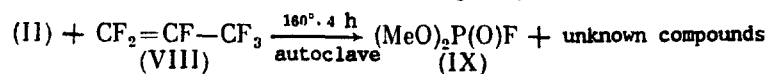
The electrophilic properties of perfluoroisobutylene (I, PFIB) are well known. In particular, the reaction of PFIB with silylated amines, accompanied by vinyl nucleophilic substitution of fluorine and the formation of fluorosilanes has been described by Zeifman et al. [1]. N-Silylphosphazenes, which are a type of secondary silylamines, have not been studied in their reaction with PFIB and other perfluoroolefins.

We have found that PFIB reacts in the cold without solvent with N-trimethylsilylphosphazenes to give previously unreported N-perfluoroisobutenylphosphazenes.

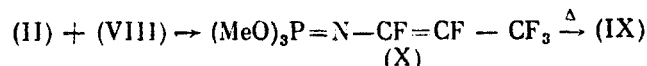


Products (V)-(VII) are liquids stable at room temperature. Products (V) and (VI) may be distilled in vacuum, while triamide (VII) decomposes upon distillation. The ^{31}P NMR signal of all the products is seen at from -1.5 to +26 ppm as a doublet with $J_{P-F} = 25-32$ Hz.

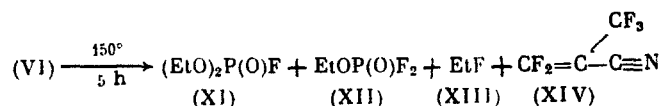
In an attempt to carry out the analogous reaction with perfluoropropylene (VIII, PFP), which is a weaker electrophile, we found that the reaction proceeds under much more vigorous conditions. Dimethyl fluorophosphate (IX) is the major phosphorus-containing product.



We assume that perfluoropropenylphosphazene (X) is formed as an intermediate, which is unstable under the experimental conditions and decomposes thermally to give fluorophosphate (IX).



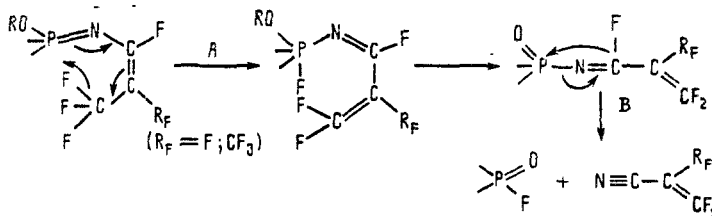
In order to confirm this scheme in the case (VI), we studied the thermal decomposition of N-perfluoroisobutenylphosphazenes (V)-(VII) and established that the major product in the thermolysis of (VI) is diethyl fluorophosphate (XI). Ethyl difluorophosphate (XII) is also formed in small amounts.



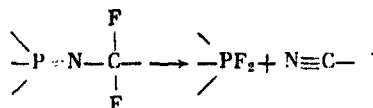
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Nitrile (XIV) was isolated only in a mixture with fluoroethane (XIII). Thus, its structure was demonstrated by ^{19}F NMR and IR spectroscopy (see Experimental).

We propose the following scheme of this reaction entailing the transfer of two fluorine atoms from perfluoroalkenyl radical by phosphorus.



The anomalously high mobility of the fluorine atoms in the α -position relative to trivalent nitrogen, has been reported for α -fluoroalkylamines [2]. We previously described the unique nucleophilic substitution of nitrogen by fluorine in a phosphaza compound with similar structure [3].



The unusual feature of the thermal decomposition of alkenylphosphazenes described above lies in the circumstance that one of the fluorine atoms is transferred not from the α position but rather from the γ position relative to nitrogen. This is undoubtedly a case of vinylogy.

EXPERIMENTAL

The ^1H , ^{19}F , and ^{31}P NMR spectra were taken on a Bruker CXP-200 spectrometer at 200, 188, and 81 MHz, respectively, relative to TMS, $\text{CF}_3\text{CO}_2\text{H}$, and H_3PO_4 as the standards. Starting phosphazenes (II)-(IV) were synthesized according to Flindt et al. [4].

General Procedure for the Preparation of Phosphazenes (V)-(VII). The calculated amount of PFIB was condensed into a flask equipped with a dropping funnel, stirrer, thermometer, and gas inlet tube at -70°C and, then, an equimolar amount of phosphazene (II)-(IV) was added slowly with constant stirring. The reaction mixture was stirred for 15 min at -50°C and 15 min at -25°C and then brought to room temperature.

Phosphazene (V) was obtained in 71% yield, bp $78-80^\circ\text{C}$ (1 mm), n_D^{22} 1.3880. PMR spectrum (δ , ppm): 3.78 d ($J_{\text{P-H}} = 14$ Hz). ^{19}F NMR spectrum (δ , ppm): 42.75 m (1F), 22.75 m (3F) 20.75 m (3F). ^{31}P NMR spectrum: 2.20 d ($J_{\text{P-F}} = 25$ Hz). Found: C, 26.34; H, 2.62; P, 9.64%. Calculated: C, 26.33; H, 2.82; P, 9.72%.

Phosphazene (VI) was obtained in 70% yield, bp $88-90^\circ\text{C}$ (1 mm), n_D^{15} 1.3932. PMR spectrum (δ , ppm): 1.41 t (9H, $^3J_{\text{H-H}} = 9.09$ Hz), 4.27 m (6H). ^{19}F NMR spectrum: 44.48 m (1F), 23.18 m (3F), 21.40 m (3F). ^{31}P NMR: -1.52 d ($J_{\text{P-F}} = 26.9$ Hz). Found: P, 8.61%. Calculated: P, 8.70%.

Phosphazene (VII): PMR spectrum (δ , ppm): 2.53 d ($J_{\text{P-H}} = 10$ Hz). ^{19}F NMR spectrum: 49.95 m (1F), 24.52 m (3F), 22.38 m (3F). ^{31}P NMR spectrum: 25.56 d ($J_{\text{P-F}} = 31.7$). This compound decomposes upon distillation.

Thermolysis of Phosphazene (VI). A sample of 4.6 g phosphazene (VI) was added to a two-necked flask equipped with a reflux condenser, calcium chloride tube, and outlet to a low-temperature trap at -70°C . The reaction mixture was heated at 150°C for 5 h. A transparent, colorless liquid consisting mainly of fluoroethane (XIII) and nitrile (XIV) began to condense in the low-temperature flask 1.5 h after the onset of the reaction. Condensation continued for 2 h. Fluoroethane (XIII): PMR spectrum (δ , ppm): 1.3 d.t (3H, $^3J_{\text{H-H}} = 7$, $^3J_{\text{H-F}} = 26$ Hz), 4.4 d.q ($^3J_{\text{H-H}} = 7$, $^2J_{\text{H-F}} = 46$ Hz). ^{19}F NMR spectrum: -135.4 m.

Perfluoromethacrylonitrile (XIV): ^{19}F NMR spectrum: 17.1 m (3F), 20.5 d.q (1F, $^2J_{\text{F-F}} = 41$, $^4J_{\text{F-F}} = 9.5$ Hz), 21.9 d.q (1F, $^2J_{\text{F-F}} = 41$, $^4J_{\text{F-F}} = 18.2$ Hz).

^{31}P NMR spectroscopy indicated that the flask residue consisted of fluorophosphate (XI) (δ_{P} : -8.6 d, $J_{\text{P-F}} = 974$ Hz) and a small amount of difluorophosphate (XII) (δ_{P} : -19.4 t, $J_{\text{P-F}} = 1013$ Hz). The distillation of this residue gave 1.84 g (92.5%) (XI).

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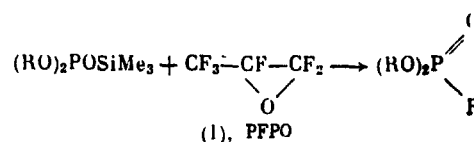
FLUORINATION OF DERIVATIVES OF TRI- AND PENTAVALENT PHOSPHORUS ACIDS BY PERFLUOROPROPYLENE OXIDE

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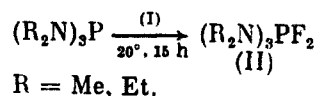
Perfluoropropylene (I) efficiently fluorinates esters and ester anhydrides of P^{III} and P^V acids to give acid fluoride derivatives of pentavalent phosphorus acids. Phosphites are initially oxidized to the corresponding phosphoryl compounds with subsequent substitution of the oxygen by two fluorine atoms by means of excess oxide (I).

We have recently shown that perfluoropropylene oxide (I, PFPO) efficiently fluorinates silyl esters of dialkyl phosphites [1].

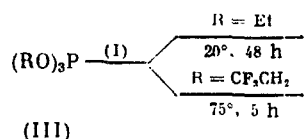


R = Me, Et, Pr.

There is no other information in the literature on the capacity of PFPO to act as oxidative fluorinating agent for P^{III} compounds. Kadyrov et al. [2] have reported the reaction of phosphites with (I) under extremely vigorous conditions but these authors gave data only on the structure and composition of the organofluorine products without investigating the fluorine-containing products. We have studied the properties of (I) as a new fluorinating agent and established that (I) fluorinates triamidophosphites under mild conditions to the corresponding difluorophosphoranes.



^{31}P NMR spectroscopy indicates that the reaction mixture when R = Et consists exclusively of phosphorane (II). When R = Me, up to 20% of an unidentified compound with a doublet at δP 41 ppm ($J_{P-F} = 956$ Hz) is present in the reaction mixture. This compound is not a product of the decomposition of phosphorane (II) (R = Me) since this phosphorane is not altered upon heating at 110°C for 4 h. Phosphites react analogously but the composition of the products is more complex due to subsequent elimination of alkyl fluorides and substituent exchange.



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