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

S. A. Lermontov, I. M. Rakov,
and I. V. Martynov

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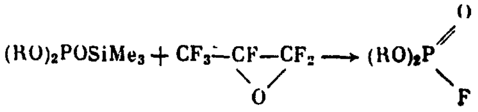
Perfluoropropylene (I) efficiently fluorinates esters and ester anhydrides of P^{III} and P^{V} acids to give acid fluoride derivatives of pentavalent phosphorus acids. Phosphites are initially oxidized to the corresponding phosphoryl compounds with subsequent substitution of the oxygen by two fluorine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

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



(I), PFPO

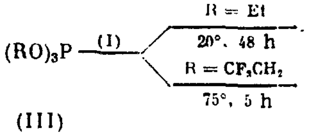
R = Me, Et, Pr.

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.

$$(R_2N)_3P \xrightarrow[20°,\ 15\ h]{(I)} \underset{(II)}{(R_2N)_3PF_2}$$

$$R = Me,\ Et.$$

^{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.



(III)

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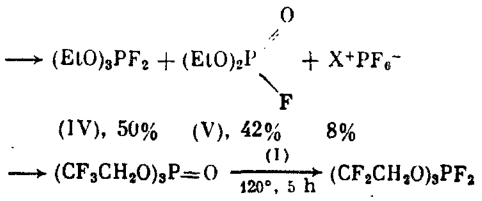
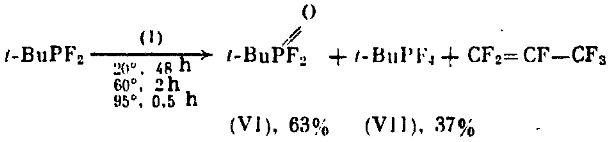


$$\longrightarrow (EtO)_3PF_2 + (EtO)_2P(O)F + X^+PF_6^-$$
$$(IV),\ 50\% \quad (V),\ 42\% \quad 8\%$$
$$\longrightarrow (CF_3CH_2O)_3P{=}O \xrightarrow[120^\circ,\ 5\ h]{(I)} (CF_2CH_2O)_3PF_2$$

X^+ - is a cation not containing phosphorus.

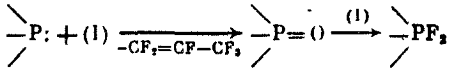
The reduced reactivity of phosphite (III, R = CF_3CH_2) in this fluorination reaction is undoubtedly related to the high electronegativity of the trifluoroethoxy substituents. In order to confirm this substituent effect, we carried out the reaction of oxide (I) with fluoroanhydrides of P^{III} acids. No reaction was noted between isobutyl difluorophosphite and (I) upon heating at 70°C for 5 h.

Tert-butyldifluorophosphine undergoes only 35% conversion upon reaction with (I) even upon prolonged contact. The reaction mixture consists of the products of oxidation (VI) and fluorination (VII).



$$t\text{-}BuPF_2 \xrightarrow[\substack{20^\circ,\ 48\ h\\ 60^\circ,\ 2\ h\\ 95^\circ,\ 0.5\ h}]{(I)} t\text{-}BuP(O)F_2 + t\text{-}BuPF_4 + CF_2{=}CF{-}CF_3$$
$$(VI),\ 63\% \quad (VII),\ 37\%$$

Perfluoropropylene was identified by gas chromatography among the products. These results indicate that the fluorination of P^{III} compounds by oxide (I) is a two-step reaction. The first step involves the oxidation to a phosphoryl compound, while the second step involves the substitutive fluorination of the phosphoryl group.



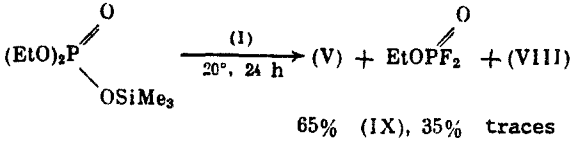
$$>P{:} + (I) \xrightarrow[-CF_2=CF-CF_3]{} >P{=}O \xrightarrow{(I)} >PF_2$$

The fluorination step holds undoubted interest since the cleavage of the P=O bond occurs with difficulty. In particular, heating with SF_4 is usually employed for the fluorination [3]. Only one reaction has been reported, in which oxide (I) acts as a fluorinating agent by reacting with hexamethylphosphorotriamide [4].

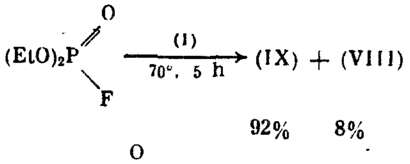
$$(Me_2N)_3P{=}O \xrightarrow[-30^\circ]{I} (Me_2N)_3PF_2 + \text{oligomerization products (I)}$$

We studied the reaction of oxide (I) with a series of phosphoryl compounds in order to clarify the limits of this reagent. The fluorination reaction is general in nature and the reaction rate depends on the electronegativity of the substituents at the phosphorus atom.

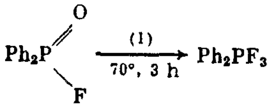
$$(EtO)_3P{=}O \xrightarrow[20^\circ,\ 10\ h]{(I)} (IV) + (V) + (EtO)_4P^+PF_6^- \qquad (a)$$
$$29\% \quad 9\% \quad (VIII),\ 62\%$$



$$(EtO)_2P(O)OSiMe_3 \xrightarrow[20^\circ,\ 24\ h]{(I)} (V) + EtOP(O)F_2 + (VIII) \qquad (b)$$
$$65\% \quad (IX),\ 35\% \quad \text{traces}$$



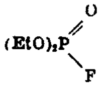
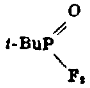
$$(EtO)_2P(O)F \xrightarrow[70^\circ,\ 5\ h]{(I)} (IX) + (VIII) \qquad (c)$$
$$92\% \quad 8\%$$



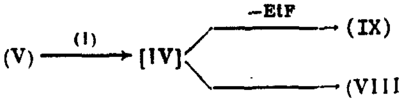
$$Ph_2P(O)F \xrightarrow[70^\circ,\ 3\ h]{(I)} Ph_2PF_3 \qquad (d)$$

$$Ph_3P{=}O \xrightarrow[20^\circ,\ 1\ h]{(I)} Ph_3PF_2 \qquad (e)$$

TABLE 1. Properties of Compounds Obtained

Compound	δP, ppm	J_{P-F}, Hz	Bp, °C (p, mm Hg)	Yield, %	Reference
$(Me_2N)_3PF_2$	−64,1 t	697	50–55° (10)	49	[6]
$(Et_2N)_3PF_2$	−58,8 t	696	43–49° (0,02)	56	[6]
$(EtO)_3PF_2$	−74,3 t	725			[7]
 $(EtO)_2P(O)F$	−8d	972			[8]
$(CF_3CH_2O)_3P{=}O$	−2.2				[9]
$(CF_3CH_2O)_3PF_2$	−73,8 t	760			[10]
 $t\text{-}BuP(O)F_2$	32 t	1183			[11]
$t\text{-}BuPF_4$	−30.2 m	1034			
$(EtO)_4P^+PF_6^-$	−1,5 s −143.7 m	693			[5]
 $EtOP(O)F_2$	−19,2 t	1010	83–87	60	[9]
Ph_2PF_3	−34,3 d.t	840 [a] 1002 [e]	85–91° (0.3)	40	[12]
Ph_3PF_2	−54,3 t	664			[13]

The formation of products (VIII) and (IX) in reactions (a) and (b) is explained by the subsequent fluorination of diethyl fluorophosphate (V), as in reaction (c), to the unstable diethoxytrifluorophosphorane and decomposition of the latter.



[5]

These results indicate that perfluoropropylene oxide (I) is an oxidative fluorinating agent for P^{III} compounds and also efficiently replaces the phosphoryl group by a $>PF_2$ group. The substituent effect on the reaction rate indicates primary nucleophilic attack by the phosphorus or oxygen atoms of the phosphoryl group on (I).

EXPERIMENTAL

The ^{31}P NMR spectra were obtained on a Bruker CXP-200 spectrometer at 81 MHz relative to 85% H_3PO_4. The gas chromatographic analysis was carried out on an LKhM-8MD chromatograph using a 2.5-m column packed with Poropak Q as the stationary phase.

General Experimental Procedure. A sample of 0.01-0.02 mole organophosphorus compound was placed into a steel test tube and a 2-3-fold excess PFPO (I) was condensed upon cooling. The tube was sealed and maintained under the conditions indicated in the text. The reaction mixture was analyzed by ^{31}P NMR spectroscopy and, when necessary, distilled. The physical constants and spectral indices of the products are given in Table 1.

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