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Fluorination of phosphorus(+3) derivatives by xenon difluoride

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Abstract

Xenon difluoride, XeF_2, effectively fluorinates various phosphorous acid derivatives as well as hydrophosphoryl compounds. Arbuzov rearrangement is followed by i-Bu→t-Bu isomerization in the case of i-Bu OPF_2.

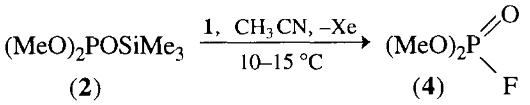
Introduction

Xenon difluoride (**1**) is a powerful and versatile reagent for the oxidative fluorination of organic and elementorganic compounds [1]. In particular, it has been shown to be an effective reagent for the fluorination of phosphines and halogenophosphines [2]. However, the reaction of **1** with phosphites and hydrophosphoryl compounds has not been described in the literature and the goal of this paper is to fill that gap.

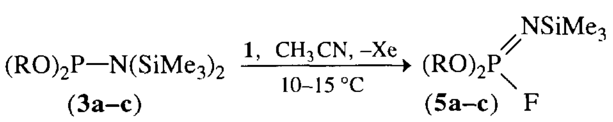
Results and discussion

A. Reaction with phosphites

We have found that reagent **1** reacts readily with derivatives of phosphorous acid such as the silyl esters **2** and amides **3**, with formation of corresponding dialkylfluorophosphates **4** or dialkylfluorophosphazenes **5**.



$$\underset{(\mathbf{2})}{(MeO)_2POSiMe_3} \xrightarrow[10\text{–}15\ ^\circ C]{\mathbf{1},\ CH_3CN,\ -Xe} \underset{(\mathbf{4})}{(MeO)_2P(=O)F}$$



$$\underset{(\mathbf{3a\text{–}c})}{(RO)_2P{-}N(SiMe_3)_2} \xrightarrow[10\text{–}15\ ^\circ C]{\mathbf{1},\ CH_3CN,\ -Xe} \underset{(\mathbf{5a\text{–}c})}{(RO)_2P(=NSiMe_3)F}$$

(**a**) R = Et; (**b**) R = iPr; (**c**) R = $-CH_2CH_2-$

Both reactions are easily monitored by the amount of evolved xenon; the products (with the exception of **5c**) were isolated by distillation. Compound **5c** appeared to be unstable and was identified only by ^{31}P NMR spectroscopy {$\delta P = +2$ ppm [d, $J(P-F) = 1004$ Hz]}.

Tris(trifluoroethyl)phosphite (**6**) reacts with reagent **1** in an unexpected manner to give two products in the ratio 4.6:1 (determined by ^{31}P NMR spectroscopy). The major product is the corresponding difluorophosphorane **7** and the minor product is the phosphonium salt **8a**.

$$\underset{(\mathbf{6})}{(CF_3CH_2O)_3P} + \underset{(\mathbf{1})}{XeF_2} \longrightarrow \underset{(\mathbf{7})}{(CF_3CH_2O)_3PF_2} + \underset{(\mathbf{8a})}{(CF_3CH_2O)_4P^+\ PF_6^-}$$

We explain the formation of the unexpected salt **8a** by fluorine exchange between **7** and XeF_2, followed by disproportionation of the transient trifluorophosphorane **9**.

$$(RO)_3PF_2 + XeF_2 \longrightarrow \underset{(\mathbf{9})}{[(RO)_2PF_3]} + [FXeOR]$$

$$2\underset{(\mathbf{9})}{[(RO)_2PF_3]} \longrightarrow \underset{(\mathbf{8})}{(RO)_4P^+\ PF_6^-}$$

The instability of dialkoxytrifluorophosphoranes of type **9** and their rapid isomerization into salts of type **8** has been described in the literature [3]. In order to confirm this mechanistic scheme, we performed the reaction of XeF_2 with the specially prepared phosphorane **7** and obtained salt **8a**.

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B. Reaction with fluorophosphites

Diethylfluorophosphite (**10**) reacts readily with XeF$_2$ giving the phosphonium salt **8b**.

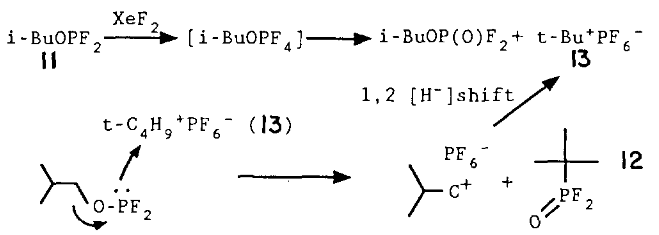
$$\underset{(\mathbf{10})}{(EtO)_2PF} + XeF_2 \xrightarrow{-Xe} [(EtO)_2PF_3] \longrightarrow \underset{(\mathbf{8b})}{(EtO)_4P^+\ PF_6^-}$$

An unusual reaction was observed when isobutyldifluorophosphite (**11**) was allowed to react with catalytic amount of XeF$_2$ (10 mol%). Surprisingly, the major product of this reaction appeared to be t-butyldifluorophosphonate (**12**) (more than 85%, according to ^{31}P NMR spectroscopy)

$$\underset{(\mathbf{11})}{i\text{-}BuOPF_2} + XeF_2 \longrightarrow \underset{(\mathbf{12})}{t\text{-}BuP(O)F_2}$$

The isolated yield of **12** exceeded 50%. Traces of isobutyldifluorophosphate, i-BuOP(O)F$_2$, were also found in the reaction mixture (^{31}P NMR). In summary, this process may be classified as an Arbuzov rearrangement accompanied by isomerization of the primary alkyl radical into a tertiary one.

To rationalize this transformation, one should keep in mind that the disproportionation of ROPF$_4$ into a mixture of ROP(O)F$_2$ and R$^+$ PF$_6^-$ is documented in the literature [4]. Thus, we believe that the initiation step is the formation of the salt **13**, which is the real catalyst of the isomerization and is regenerated in accordance with the general scheme of an Arbuzov rearrangement.



We believe that such reactions may give easy access to tertiary phosphonates of type **12** and their derivatives.

C. Reaction with hydrophosphoryl compounds

It is known that alkyl- and dialkyl(aryl)-phosphines are fluorinated by XeF$_2$ with conservation of the P–H bond [2]. We have found that diphenylphosphinic acid (**14**) readily reacts with XeF$_2$ giving the corresponding fluoroanhydride **15**.

$$\underset{(\mathbf{14})}{Ph_2P(O)H} + XeF_2 \longrightarrow \underset{(\mathbf{15})}{Ph_2P(O)F}$$

Dialkylphosphites **16** react with XeF$_2$ very slowly in the absence of catalyst but much more rapidly in the presence of pyridine or BF$_3$·Et$_2$O. However, these reactions are non-selective and cannot be used for the synthesis of dialkylfluorophosphates.

$$\underset{(\mathbf{16})}{(RO)_2P(O)H} \xrightarrow{1} \underset{(5\%\text{–}10\%)}{(RO)_2P(O)F} + 5\text{–}7 \text{ unidentified products}$$

R = Me, Et, Pr

Experimental

^1H and ^{31}P spectra were recorded on a Brucker CXP-200 instrument (200 and 81 MHz, respectively) with TMS and 85% H$_3$PO$_4$ as external standards. Chemical shifts are reported in δ units (ppm) downfield from the reference.

A general procedure for the fluorination of (MeO)$_2$POSiMe$_3$ (2), (RO)$_2$PN(SiMe$_3$)$_2$ (3a–c) and (EtO)$_2$PF (10)

Phosphorus compound (2–3 mmol) was added dropwise to a cooled (0–5 °C), stirred solution of an equivalent amount of XeF$_2$ in 3–5 ml of dried CH$_3$CN. After completion of gas evolution, the reaction mixture was stirred at room temperature for 30–40 min, analyzed by ^{31}P NMR spectroscopy with a product being capable of isolation by distillation (except **5c** and **8b**). The following compounds were obtained:

Compound (**4**): B.p. 63–65 °C/15 mmHg (55%). ^{31}P NMR δ: -5.5 [d, J(P–F) = 972 Hz] ppm. Lit. value [5]: b.p. 149 °C/760 mmHg.

Compound (**5a**): B.p. 60–62 °C/18 mmHg (50%). ^{31}P NMR δ: -12 [d, J(P–F) = 960 Hz] ppm. Lit. value [6]: b.p. 63–65 °C/20 mmHg. ^{31}P NMR δ: -15.5 [J(P–F) = 962 Hz] ppm.

Compound (**5b**): B.p. 77 °C/20 mmHg (45%). ^{31}P NMR δ: -14 [d, J(P–F) = 959 Hz] ppm.

Compound (**8b**) (R = Et): ^{31}P NMR δ: -0.6 (s); -143 [septet, J(P–F) = 710 Hz] ppm. Lit. value [3]: ^{31}P NMR δ: -5 (s); -147 [septet, J(P–F) = 700 Hz] ppm.

Fluorination of tris(trifluoroethyl)phosphite (6)

A solution of XeF$_2$ (170 mg, 1 mmol) in CH$_3$CN was added to a cooled solution of **6** (0.33 g, 1 mmol). The reaction mixture (monitored by ^{31}P NMR) contained two substances, i.e. difluorophosphorane **7** {-77.16 [t, J(P–F) = 750 Hz] ppm} and **8a** {-2.7 (s); -143 [septet, J(P–F) = 710 Hz] ppm} in a 4.6:1 ratio. Phosphorane **7** was isolated by distillation, b.p. 59–61 °C/10 mmHg (58% yield). Lit. value [7]: ^{31}P NMR δ: -77.3 [J(P–F) = 747 Hz] ppm.

Reaction of XeF_2 with isobutyldifluorophosphite (11)

XeF_2 (0.24 g, 1.4 mmol) was added to 2 g (14 mmol) of **11** at −30 °C (no reaction occurred at this temperature) and the cooling bath was slowly heated. When the bath temperature reached −10 to −12 °C, a vigorous reaction occurred accompanied by gas evolution. After completion of the reaction, the mixture consisted (according to ^{31}P NMR) of 85%–90% of phosphonate **12**, 10% of PF_6^- anion and traces of i-$BuOP(O)F_2$ {^{31}P NMR δ: −19 [t, $J(P-F) = 1010$ Hz] ppm}. Phosphonate **12** was purified by distillation, b.p. 120 °C (1.05 g, 52.5%). ^{31}P NMR δ: 31.95 [triplet of decets, $J(P-F) = 1172$ Hz, $J(P-H) = 19$ Hz] ppm. ^1H NMR δ: 1.3 [dt, $J(H-P) = 19$ Hz, $J(H-F) = 1$ Hz] ppm. Lit. value [8]: b.p. 63 °C/85 mmHg.

Fluorination of $Ph_2P(O)H$ (14)

A solution consisting of 220 mg (1.3 mmol) of XeF_2 in 1.5 ml CH_3CN was added dropwise to a mixture of 263 mg (1.3 mmol) of **14**, 100 μl of pyridine and 1 ml of CH_3CN. The exothermic reaction was completed within 5–10 min. The mixture was stirred for 1–1.5 h and evaporated. The residue obtained was practically pure **15**. ^{31}P NMR δ: 41 [d, $J(P-F) = 1013$ Hz] ppm. Lit. value [9]: ^{31}P NMR δ: 40 (d, $J = 1020$ Hz) ppm.

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