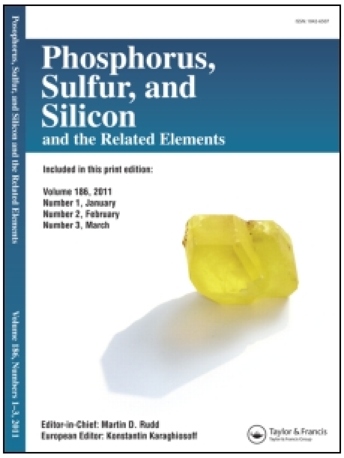

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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To cite this Article Konieczko, Witold T. , Łopusiński, Andrzej and Michalski, Jan(1989) 'COMMUNICATION THIONYL FLUORIDE: A REAGENT FOR TRANSFORMATION OF DIORGANYL PHOSPHATES AND THEIR STRUCTURAL ANALOGUES INTO THE FLUORIDATES', Phosphorus, Sulfur, and Silicon and the Related Elements, 42: 1, 103 — 104
To link to this Article: DOI: 10.1080/10426508908054881
URL: http://dx.doi.org/10.1080/10426508908054881

Phosphorus, Sulfur, and Silicon, 1989, Vol. 42, pp. 103–104
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COMMUNICATION

THIONYL FLUORIDE: A REAGENT FOR TRANSFORMATION OF DIORGANYL PHOSPHATES AND THEIR STRUCTURAL ANALOGUES INTO THE FLUORIDATES†

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(Received July 25, 1988)

Organophosphorus acids and dithioacids are transformed in almost quantitative yield into the corresponding fluoridates by reaction with thionyl fluoride under very mild conditions.

Key words: Thionyl fluoride; organophosphorus fluoridates and thiofluoridates; phosphinofluoridic acid salts.

We have recently reported the application of sulfuryl chloride fluoride SO_2ClF as a highly efficient reagent for the transformation of trimethylsilylesters $RR'POSiMe_3$ of tricoordinate phosphorus acids into the corresponding fluoridates $RR'P(O)F$.[1] This reagent has also been applied in nucleotide chemistry.[2] Sulfuryl chloride fluoride can be used for the direct transformation of diorganyl phosphates into the fluoridates.[3] However, this reagent is not fully selective and some amounts of chloridates are formed in addition to the desired product. In order to find a fully selective reagent which could be applied for biologically important phosphates, we turned our attention to the readily available thionyl fluoride SOF_2.[4] This reagent has already been applied to obtain P-fluoroderivatives in moderate yield and selectivity starting from tri-coordinate phosphorus compound.[5]

Our goal, which is achieved in this work, was to use as starting materials organophosphorus acids readily available from synthetic and natural sources.

Thus, we have found that thionyl fluoride reacts with phosphorus acids **1** in the presence of triethylamine in a selective way under very mild conditions.

$$RR'P(O)OH + SOF_2 + Et_3N \xrightarrow[CH_2Cl_2]{-60^\circ C} RR'P(O)F + Et_3N \cdot HF + SO_2$$

1a $R = R' = Ph$ — **2a** $\delta^{31}P$: 39.8 ppm, J_{PF}: 1016 Hz
1b $R = R' = EtO$ — **2b** $\delta^{31}P$: 11.1 ppm, J_{PF}: 997 Hz

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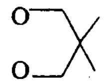
† Dedicated to Prof. Dr. Fritz Cramer on the occasion of his 65th birthday.

Without tertiary amine the reaction is slow and gives a mixture of products. Analogous reaction between dithioic acid **3** and thionyl fluoride leads to diorganyl thiofluoridates **4.**

$$RR'P(S)SH + SOF_2 + Et_3N \xrightarrow[CH_2Cl_2]{-60^\circ C} RR'P(S)F + Et_3N \cdot HF + S_n + SO_2$$

3a $R = R' = EtO$ **4a** $\delta^{31}P$: 61.4 ppm, J_{PF}: 1071 Hz

3b R,R'  **4b** $\delta^{31}P$: 52.0 ppm, J_{PF}: 1071 Hz

With dibasic acids **5** under similar conditions the reaction with thionyl fluoride leads to the monofluoridates **6.**

$$RP(O)(OH)_2 + SOF_2 + Et_3N \xrightarrow[CH_2Cl_2]{-60^\circ C} RP(O)FO^-Et_3NH + Et_3N \cdot HF + SO_2$$

5 $R = Ph$ **6** $\delta^{31}P$: 20.5 ppm, J_{PF}: 995 Hz

This reaction stops at the stage of the monofluoridate **6** even when large excess of thionyl fluoride is used.

It is most likely that all the reactions mentioned proceed via mixed anhydrides $>P(X)—O—SO—F$ ($X = O, S$) which are transformed into the fluoridates **2**, **4** and **6** either by external attack of the fluoride anion or by internal elimination. The fluoridates obtained by this method are formed in quantitative yield according to ^{31}P NMR spectroscopy.

The general procedure for the preparation of **2** and **6**, as exemplified by the preparation of 2-fluoro-2-thioxa-5,5-dimethyl-1,3,2-dioxaphosphorinane **4b**, is as follows. Freshly prepared thionyl fluoride[4] (10 mmol) was evaporated into the stirred solution of the corresponding acid (8.0 mmol) and triethylamine (8.0 mmol) in dry dichloromethane at −60°C. The reaction mixture was stirred for 3 hrs and the solvent removed in vacuo. The crude fluoridate was purified by distillation. B.p. 60°C at 0.025 mmHg. Yield 80%. Because of the high toxicity of organophosphorus fluoridates experiments must be carried out with special precautions.

ACKNOWLEDGEMENT

Support of this research by the Polish Academy of Sciences is gratefully acknowledged (Project CPBP-01-13).

REFERENCES

1. W. Dabkowski and J. Michalski, *J. Chem. Soc., Chem. Commun.*, **1987**, 755.
2. W. Dabkowski, F. Cramer and J. Michalski, *Tetrahedron Lett.*, in press 1988.
3. A. Łopusiński and J. Michalski, *Angew. Chem.*, **94**, 302 (1982).
4. C. W. Tullock and D. D. Coffman, *J. Org. Chem.*, **25**, 2016 (1960).
5. T. Mahmood and J. M. Shreeve, *Inorg. Chem.*, **24**, 1395 (1985).