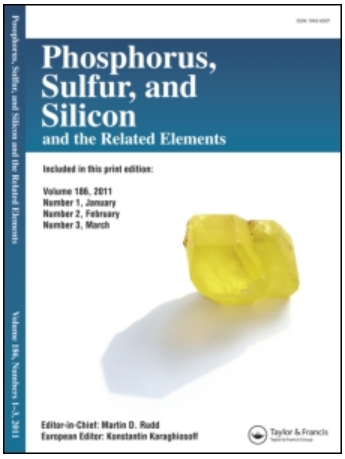

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Alkylthio-Fluoro-and Difluoromethylphosphonates: Synthesis and Reactivity

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Alkylthio-Fluoro-and Difluoromethylphosphonates : Synthesis and Reactivity

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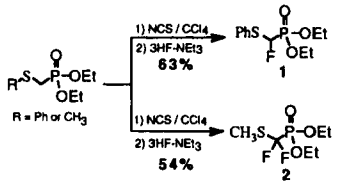
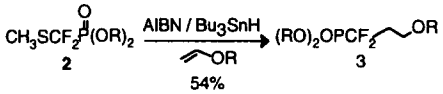
The mimicry of reactive phosphate esters has become an established in the design of biologically-active compounds. Fluoromethylene and difluoromethylene-phosphonates have been prepared as non hydrolysable analogues of nucleosides or phosphoamino-acids.We have attempted to explore a new alternative approach using free radical chemistry from alkylthiofluoromethylphosphonate **1** and alkylthiodifluoromethylphosphonate **2**. We first developped a new preparation of fluorinated alkylthiophosphonate esters using electrophilic and nucleophilic fluorine sources. Using N-fluorobenzenesulfonimide **1** could be obtained in moderate yield (@40%). On the other hand Selectfluor™ allowed to obtain the difluoromethylphosphonate **2** but in relatively low yield (@10%).Using nucleophilic fluorine source[1] ($3HF\text{-}NEt_3$) we showed that phosphonate **1** and **2** could be obtained selectively from chloro- and dichloromethylphosphonate esters. By this way, diethyl alkylsulfanyl- fluoromethylphosphonate **1** and difluoromethylphosphonate **2** were respectively synthetized in 63% and 54% yields.



Using the strategy developed by Balczewski *et al.*.[2] , difluoromethylphosphonyl radical could be generated from **2**. Its electrophilic character allowed to trape it only with electron-rich alkenes. By this way, 3-alkoxy-1,1-difluoropropylphosphonate **3** were obtained in 54% yields.



References

[1] C. Jouen, S. Lemaître, T. Lequeux, J.C. Pommelet, *Tetrahedron* **1998,** *in press.*
[2] P. Balczewski, W.M. Pietrzykowski, *Tetrahedron* **1996,** *53,* 7291–7304.