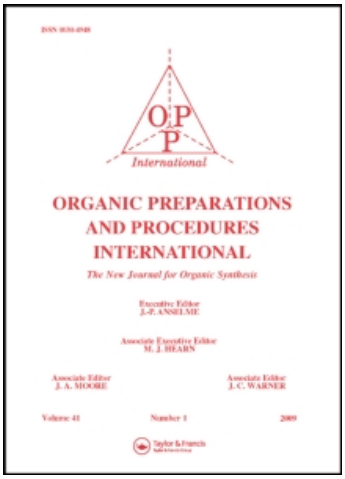

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IMPROVED SYNTHESIS OF *bis*(2,2,2-TRIFLUOROETHYL) PHOSPHOROCHLORIDATE

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IMPROVED SYNTHESIS OF *bis*(2,2,2-TRIFLUOROETHYL) PHOSPHOROCHLORIDATE

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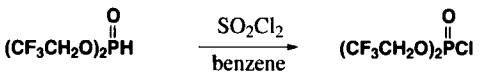
Phosphorochloridate electrophiles have found extensive applications in organic synthesis in the preparation of β-ketophosphonates,[1] α-phosphono lactones and esters,[2] ketene acetal phosphates for use in the Stille coupling,[3] and alkynes[4] amongst many other applications.[5] *bis*(2,2,2-Trifluoroethyl) phosphorochloridate (**1**) has been underutilized as a reagent in organic synthesis, due to the impracticality of the literature method of synthesis.[6] The previous synthesis involved treatment of $P(O)Cl_3$ with trifluoroethanol to yield a mixture of products which included (2,2,2-trifluoroethyl) phosphorodichloridate [$CF_3CH_2OP(O)Cl_2$ (**2**)] which was purified by vacuum distillation. The dichloridate **2** was treated further with trifluoroethanol and compound **1** was isolated after a second vacuum distillation. The problems with this route include low yields and a tedious and difficult separation *via* repeated high vacuum fractional distillations. This paper describes an efficient, one-step synthesis of **1** from commercially available reagents, which may be purified easily by distillation under aspirator or high vacuum to provide pure material in quantitative yield.



Our improved synthesis relies on the method first reported by Sosnovsky and Zaret.[7] Addition of a solution of *bis*(2,2,2-trifluoroethyl) phosphite in benzene to a solution of sulfuryl chloride in benzene results in quantitative formation of *bis*(2,2,2-trifluoroethyl) phosphorochloridate (**1**), as determined by both ^{31}P NMR spectroscopy and GC analysis. In our lab, typically the product is isolated by distillation under aspirator-induced vacuum to afford pure material.

EXPERIMENTAL SECTION

^{1}H, ^{13}C and ^{31}P NMR spectra were recorded on a 400 MHz Varian Gemini 2000 Spectrometer. *bis*(2,2,2-Trifluoroethyl) phosphite and sulfuryl chloride were purchased from Aldrich Chemical Co.

***bis*(2,2,2-Trifluoroethyl) Phosphorochloridate (1).**- To a solution of *bis*(2,2,2-trifluoroethyl) phos-

phite (50.0 g, 203 mmol) in dry benzene (55 mL) was added dropwise a solution of sulfuryl chloride (20.3 mL, 203 mmol) in benzene (55 mL) at 0°. After the addition had been completed, the mixture was allowed to warm to rt over 2 h. The solvent was removed *in vacuo* and purification by short path distillation through a 10-cm Vigreux column afforded compound **1** (52.8 g, 93%) as a clear, colorless liquid, bp. 67-70/14 mm, *lit.*[6] bp 67-68/14 mm. ^{1}H NMR ($CDCl_3$): δ 4.58-4.41 (4H, m). ^{13}C NMR ($CDCl_3$): δ 121.6 (2, dq, J = 277.0, 11.4 Hz), 64.7 (2, dq, J = 38.9, 5.3 Hz). ^{31}P NMR ($CDCl_3$): δ 6.7.

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