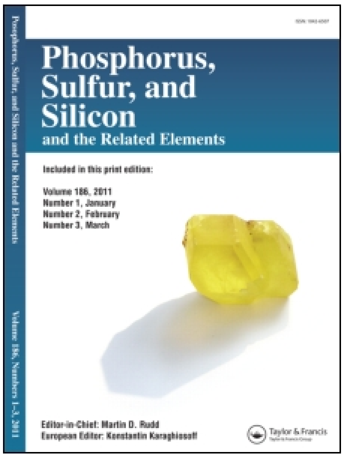

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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To cite this Article Heliński, J. , Skrzypczyński, Z. , Wasiak, J. and Michalski, J.(1990) 'A NEW EFFICIENT SYNTHESIS OF TRIFLUOROACETYL HALIDES AND MIXED ANHYDRIDES OF PHOSPHORUS AND TRIFLUOROACETIC ACIDS', Phosphorus, Sulfur, and Silicon and the Related Elements, 54: 1, 225 — 226

To link to this Article: DOI: 10.1080/10426509008042143

URL: http://dx.doi.org/10.1080/10426509008042143

Phosphorus, Sulfur, and Silicon, 1990, Vol. 54, pp. 225–226
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Communication

A NEW EFFICIENT SYNTHESIS OF TRIFLUOROACETYL HALIDES AND MIXED ANHYDRIDES OF PHOSPHORUS AND TRIFLUOROACETIC ACIDS

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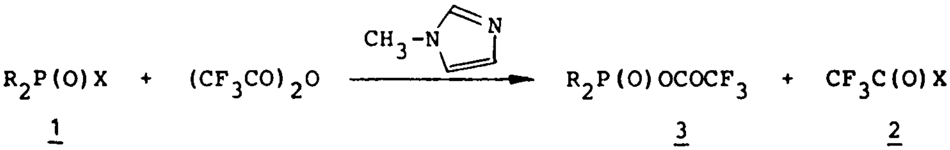
(Received April 4, 1990)

Reaction of trifluoroacetic anhydride with chloroanhydrides of phosphorus acids $R_2P(O)Cl$ results in formation of mixed anhydrides $R_2P(O)\ OCOCF_3$ and trifluoroacetic acid halides CF_3COX (X=Cl, Br, I) in quantitative yield.

Key words: Phosphoric-carboxylic acid anhydride; trifluoroacetyl halides.

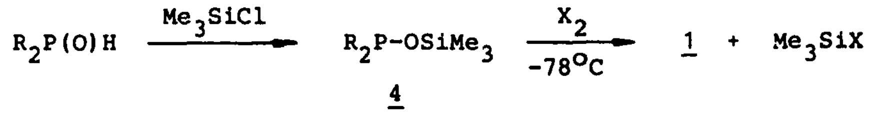
The importance of organic fluorine compounds in pure and applied chemistry has stimulated interest in the synthesis of perfluoroacetic halides. However, most synthetic methods described to this day suffer from low yield, difficult synthetic procedures, or both.[1–3] As a part of our studies on phosphorus acid anhydrides, we recently have found that trifluoroacetyl halides 2 are formed quantitatively when phosphorus acids halides 1 are allowed to react at ambient temperature with trifluoroacetic anhydride in the presence of catalytic amounts of *N*-methylimidazole.



(X=I,Br,Cl) (R=EtO,Ph)

The trifluoroacetyl halides 2 boil at low temperatures and can be readily separated from the mixed anhydrides 3. Compounds 2 can be either isolated by vacuum-line technique or directly employed for further transformations by evaporation in a stream of argon. Trifluoroacetyl iodide (b.p. 23°C) requires simple fractional distillation for purification. The structure of trifluoroacetyl halides was confirmed by ^{13}C NMR spectroscopy and quantitative transformation into the trifluoroacetanilide identical with the authentic specimen. Reaction of trifluoroacetic anhydride with dialkylphosphorofluoridates 1 (X=F) was also investigated, however, it failed to give the expected trifluoroacetyl fluoride. This result is not surprising in view of the strong P—F bond.

Phosphorochloridates 1 (X=Cl, R=R'O) are commercially available. Recently, bromidates 1 (X=Br) and iodates 1 (X=I) have become available *via* synthetic procedure devised in this Laboratory and based on the following sequence of transformations.[4]



$$R_2P(O)H \xrightarrow{Me_3SiCl} \underset{4}{R_2P\text{-}OSiMe_3} \xrightarrow[-78^oC]{X_2} 1 + Me_3SiX$$

The halidates 1 formed can be readily separated from volatile trimethylsilyl halides. The halides 1 are formed in almost quantitative yield and high purity and can be directly employed in the synthesis of trifluoroacetyl halides.

In a typical experiment the diethylphosphorochloridate 1 (X=Cl, R=EtO) was added to an equivalent amount of trifluoroacetic anhydride with exclusion of moisture. To that mixture 5% mol of *N*-methylimidazole was added and the resulting mixture was kept at room temperature overnight. Trifluoroacetyl chloride was removed in a stream of dry argon and collected by freezing. The residue consisted of almost pure mixed anhydride 3 (R=EtO), contaminated only by small amounts of *N*-methylimidazole. The anhydride derived from diphenylphosphinic acid 3 (R=Ph) was prepared by a similar procedure. Their physical and chemical properties are identical with those observed in our previous studies.[5]

Preparation of trifluoroacetyl bromide and iodide was based on an one-flask procedure starting from dialkyltrimethylsilyl phosphite 4 which was allowed to react with one equivalent of the appropriate elemental halogen at −78°C in methylene chloride solution. After evaporation of the volatile compounds, trifluoroacetic anhydride and 5% mol of *N*-methylimidazole was added and the reacting mixture was kept at room temperature overnight. Removal of the halides 2 by evaporation *in vacuo* left the anhydrides 3 of slightly lower purity than those prepared from phosphorochloridates.

Because of the ready access of reagents, mild reaction conditions, easy work-up and better yield when compared to previous methods, our procedure provides a facile access to acyl halides and phosphoric-carboxylic acids anhydrides derived from trifluoroacetic acid.

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