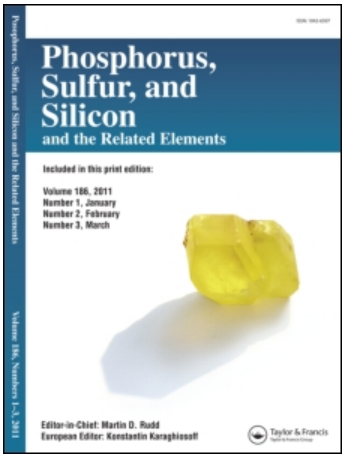

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2-CHLORO-2,4-DIOXO-3-METHYL-1,3,2-THIAZAPHOSPHOLIDINE. IS IT AN IDEAL CYCLIC PHOSPHORYLATING AGENT ?

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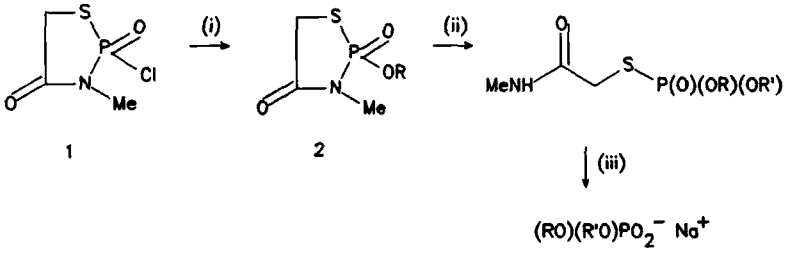
Abstract 2-Alkoxy-2,4-dioxo-3-methyl-1,3,2-thiazaphospholidines undergo facile ring-opening with Cl^-, and, in particular, with water.

INTRODUCTION

In the synthesis of unsymmetrical dialkyl phosphates, Ugi *et. al.* introduced 2-chloro-2,4-dioxo-3-methyl-1,3,2-thiazaphospholidine **1** as an ideal phosphorylating agent; its value stemming from a sequence of very selective steps of the nucleophilic cleavage of the P—Cl, the P—N, and, finally, the P—S bond (Scheme 1).[1] When applying that approach to the



1 2

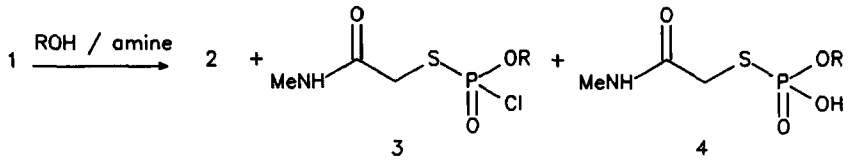
(i) ROH / amine; (ii) R'OH / catalyst; (iii) aq. NaOH

Scheme 1

preparation of some phosphate diesters, we have found that the first step of the sequence is not completely selective in terms of the retention of the thiazaphospholidine ring.[2]

RESULTS AND DISCUSSION

Substrate **1** was treated with alcohols using various bases (pyridine or triethylamine), solvents, and reaction temperatures. The reaction invariably yielded a mixture consisting of three compounds (total yield 100%), that is the required ester **2** (70-80%), and the two ring-opened products **3** (2-12%) and **4** (18-22%) (Scheme 2).



Scheme 2

Phosphorochloridate **3** *is not* a result of the nonselective reaction of an alcohol with **1** (P—N instead of the P—Cl bond cleavage). We have shown that **3** is produced by the subsequent opening of the thiazaphospholidine ring in **2** by Cl^- ion, released in the first step. Similarly, acid **4** was formed *via* an extremely facile hydrolytic ring opening of the cyclic ester **2**. In general, we found that the reaction of **1** with nucleophiles (alcohols, amines, *etc*) gives in addition to the expected substitution product some quantities of the product resulting from the subsequent attack of Cl^- at the P—N bond of the ring. The hydrolytic sensitivity of the ring in **2** is remarkable; we found esters **2** exceptionally hygroscopic, so the work with 1,3,2-thiazaphospholidine derivatives requires most rigorous exclusion of moisture. That property may limit the application of such compounds in selective phosphorylations.

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