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A convenient phosphoryloxylactonization of pentenoic acids with (diacetoxyiodo)benzene

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Abstract

The convenient one-pot method for phosphoryloxylactonization of alkenoic acids was reported: when (diacetoxyiodo)benzene, various 4-pentenoic acids and phosphates were mixed in CH_3CN at room temperature, phosphoryloxylactones were obtained in good to excellent yields in short times, some had two diastereoisomers.
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Keywords: Phosphoryloxylactonization; (Diacetoxyiodo)benzene; Alkenoic acid; Synthesis

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Hypervalent iodine reagents have found broad application in organic chemistry and nowadays frequently used in synthesis due to they are nonmetallic oxidation reagents and avoid the issues of toxicity of many transition metals commonly involved in such processes [1–10]. Using hypervalent iodine reagents some special phosphate esters which are important in organic chemistry as well as biochemistry have been prepared: Stang and his workers reported the first alkynyl phosphates synthesis in 1987 [11]; Koser *et al.* also prepared a novel hypervalent iodine reagent, [hydroxy((bis(phenyloxy)phosphoryl)oxy)iodo]benzene, and found that it can react with 4-pentenoic acids and three phosphoryloxylactones were obtained [12]. However, the yields of Koser's reaction were middle or poor and the reaction needed several hours; moreover, the number of phosphoryloxylactones was only three till now. In order to improve the yield, short the reaction time and find a convenient method to prepare more and important phosphoryloxylactones, we have investigated the reaction of alkenoic acids, (diacetoxyiodo)benzene and phosphates. Here we would like to report a fast and convenient one-pot method for phosphoryloxylactonization of alkenoic acids, a series of new 5-phosphoryloxy-4-pentanol-actones were synthesized.

We first investigated the ''one-pot'' procedure to improve Koser's method due to the preparation of [Hydroxyl((bis(phenyloxy)phosphoryl)oxy)iodo]benzene and its reaction with 4-pentenoic acids were separated in two steps. When equal equivalent of (diacetoxyiodo)benzene, diphenyl phosphate and 4-pentenoic acid were mixed in CH_3CN at room temperature and stirred, we found that only after 1 h the reaction was completed, giving the desired 5-(bis(phenyloxy)phosphoryl)oxy-4-pentanolactone in 85% of yield (Scheme 1). Prompted by the result, a series of experiments were performed on the reaction of 4-pentenoic acid with (diacetoxyiodo)benzene and diphenyl phosphate

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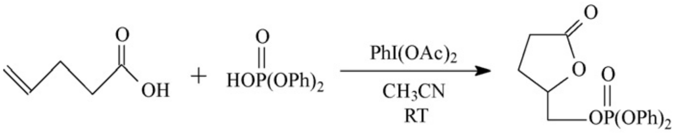
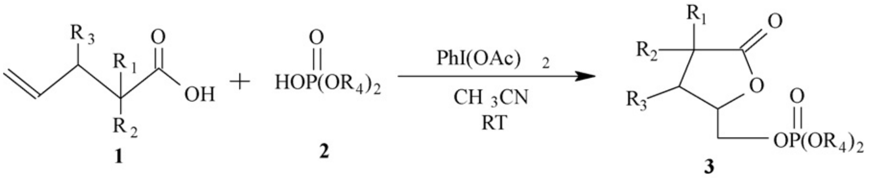


Scheme 1. .



Scheme 2. .

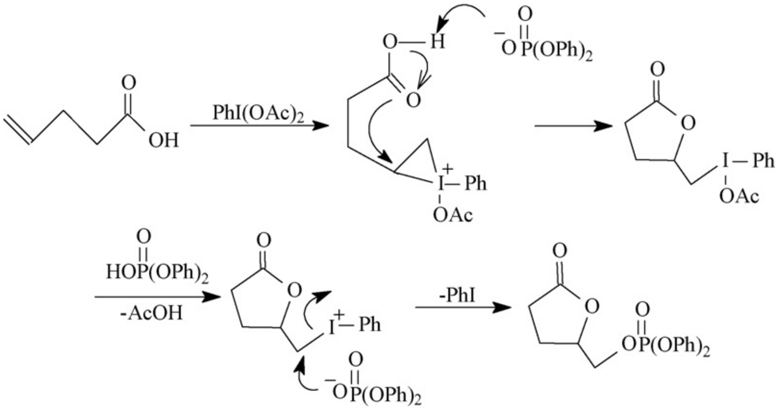
to determine the suitable reaction conditions, and CH_3CN was found to be the most preferred solvent. When CF_3CH_2OH was used in place of CH_3CN, the reaction gave product in 60% of yield. Other solvents, such as CH_2Cl_2, CH_3OH and DMF were not effective, the reaction occurred slowly and afforded the product with poor yields.

Under the optimum reaction conditions, the reaction of a series of alkenoic acids (**1**) with phosphates (**2**) and (diacetoxyiodo)benzene in CH_3CN at room temperature were investigated, several 5-phosphoryloxy-4-pentanolactones (**3**) were provided, most of them were new compounds (Scheme 2), which were characterized by ^{1}H NMR, ^{13}C NMR, IR, MS spectra and melting points, the good results are summarized in Table 1.

It is shown from Table 1 that 4-pentenoic acids easily reacted with phosphates and (diacetoxyiodo)benzene, a serious of 5-phosphoryloxy-4-pentanolactones with good yields were obtained in 1–2 h. Similar treatment of 5-hexenoic acid, the desired product of 6-phosphoryloxy-5-hexanolactone was found from the crude product in middle yield by ^{1}H NMR technique, but it decomposed during purification, which agreed with Koser's report that it was unstable [12]. We also checked 3-butenoic acid, *trans*-3-hexenoic acid and 2-cyclopentene-acetic acid under the optimum reaction conditions, unfortunately, only the corresponding unsaturated lactones were obtained.

Koser found when 2-methyl-4-pentenoic acid **1b** was treated with the hypervalent iodine reagent, a mixture of diastereomers was obtained, the ratio varied from 1.2 to 1.4:1 [12]. In our reaction protocol, we also found when **1b** was used, the corresponding products were mixture of diastereomers, the ratio was 2.9:1, which was determined by examination of the ^{1}H NMR spectra of phosphoryloxylactones; while 3-methyl-4-pentenoic acid **1c** was treated in the reaction, the ratio for the obtained mixture of diastereomers was nearly1:1, which meant that **1b** had better stereoselectivity than **1c**.

The proposed mechanism for the one-pot phosphorylactonization of alkenoic acids is similar to the literature procedure (Scheme 3) [13], which included the electrophilic addition of (diacetoxyiodo)benzene on the double bond,



Scheme 3. .

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