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Synthesis and herbicidal activities of methyl-1-(2,4-dichlorophenoxyacetoxy)alkylphosphonate monosalts

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Abstract

A series of 1-(2,4-dichlorophenoxyacetoxy)alkylphosphonic acid dimethyl esters **5** and its corresponding phosphonate monosalts **6** were synthesized as potential herbicide. The phosphonate monosalts can be prepared from 1-(2,4-dichlorophenoxyacetoxy)alkylphosphonic acid dimethyl esters **5**, which were synthesized by the condensation of *O*,*O*-dimethyl-1-hydroxyalkylphosphonates with dichlorophenoxyacetic chloride. This method provides a simple and efficient procedure for the synthesis of phosphonate derivatives containing sensitive groups to acid, base or water such as carboxylate ester bond; and the herbicidal activity of title compounds was evaluated in a set of experiments in greenhouse. Most of the compounds exhibited notable herbicidal activity.

Keywords: Alkylphosphonate; Monosalt; 1-Hydroxyalkylphosphonate; Synthesis; Herbicidal activity

1. Introduction

One approach to design an inhibitor of pyruvate dehydrogenase (PDH) with a novel structure by using biochemical reasoning was attempted. A series of α-oxophosphonic acid derivatives have been investigated in recent years [1]. Some substituted phenoxyacetoxyalkylphosphonates have shown good herbicide activities and demonstrated as an inhibitor of PDH in our previous work [2,3]. Its corresponding phosphonate monosalts would be of better herbicidal activity, because the structure of the salt is more analogous to the pyruvate which acts as the substrate of pyruvate dehydrogenase complex. In order to find new phosphonate derivatives with better herbicidal activity, the sodium and potassium structural unit was introduced into phosphonates molecules, so we are interested in extending our investigations to a novel series of methyl 1-(dichlorophenoxyacetoxy)alkylphosphonate monosalts and finding a mild and efficient method for conversion of dimethyl phosphonates to corresponding phosphonate monosalts. Here we report the preparation of 1-(2,4-dichlorophenoxyacetoxy)alkylphosphonate monosalts and their herbicidal activity against *Echinochloa crusgalli* Beava, *Digitaria sanguinalis* Scop, *Brassica napus* L., *Amaranthus retroflerus* L., and *Medicago sativa* L.

2. Results and discussion

2.1. Synthesis of 1-(2,4-dichlorophenoxyacetoxy)-alkylphosphonate monosalts

The title compounds were synthesized by means of the multi-step procedure outlined in Scheme 1.

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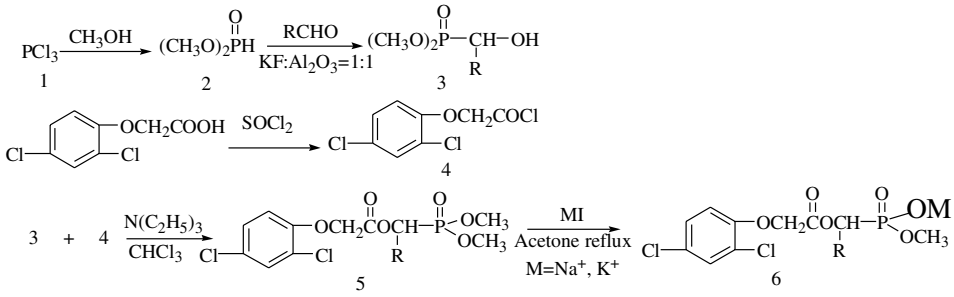
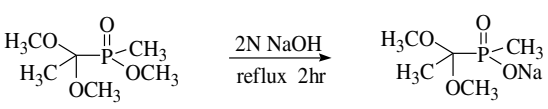


Scheme 1.

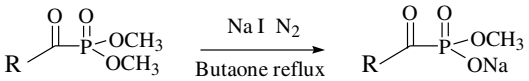
We chose a convenient route to obtain the title compounds **6a**–**j** starting from dimethyl phosphite, which was used directly as obtained commercially or prepared by the reaction of phosphorus trichloride and methanol. Dimethyl phosphite reacted with aldehydes to give *O*,*O*-dimethyl-1-hydroxyalkylphosphonates **3**. The title compounds can be obtained from 1-(2,4-dichlorophenoxyacetoxy)alkylphosphonic acid dimethyl esters **5**, which were prepared by the condensation of *O*,*O*-dimethyl-1-hydroxyalkylphosphonates **3** with dichlorophenoxyacetic chloride **4**.

Phosphonate or phosphinate monosalts could be generally synthesized from corresponding phosphonate or phosphinate derivatives by several procedures [4], such as some phosphinate salts could be obtained by a direct means of converting the phosphinate ester into the corresponding phosphinate salts in 2N sodium hydroxide solution (Eq. (1)). However, the method is not applicable to prepare the phosphonates containing sensitive groups to acid, base, water or temperature such as carboxylate ester group. We failed to obtain the title compounds by direct reaction of converting the phosphonate into the corresponding phosphonate salts in sodium hydroxide solution. We observed that carboxylate ester bond in 1-(2,4-dichlorophenoxyacetoxy)alkylphosphonates **5** or title compounds **6** were easily cleaved by hydrolysis in the presence of base and water at about 60 °C. For example, when the title compound **6b** was prepared under basic (pH 9–10) condition by the reaction in Scheme 1, both methyl-1-hydroxyethylphosphonate monosodium and 2,4-dichlorophenoxyacetic acid as the by-product were found and identified, respectively.



(1)

We also attempted to prepare the title compound **6** by a direct reaction of 1-hydroxyalkylphosphonates monosalt with 2,4-dichlorophenoxyacetic chloride in the presence of pyridine, but unfortunately it was not a good way to prepare the title compounds in better yields. Therefore, as described in the literature [4] (Eq. (2)), the metallic iodide appears to be the best choice for the preparation of phosphonate monosalts from corresponding phosphonates.



(2)

Based on the above considerations, the synthetic route (Scheme 1) was chosen to prepare the phosphonate monosalts. The experiment showed that the reactions of the compounds **5a**–**f** with sodium iodide or potassium iodide were affected by reaction temperature, base, solvent and water. We attempted to prepare the title compound **6h** by the reaction of **5h** with oven-dried potassium iodide in the presence of butanone for 36 h, but no title compound **6h** was found, only producing corresponding methyl-1-hydroxyethylphosphonate monopotassium and 2,4-dichlorophenoxyacetic acid as by-product instead. However, the compound **5h** and potassium iodide were dissolved in acetone and the solution stirred and refluxed only for 12 h, the title compound **6h** could be obtained.

Therefore, in the molecular structure of *O*,*O*-dimethyl-1-(2,4-dichlorophenoxyacetoxy)alkylphosphonates, the carboxylate ester bond may be more delicate to cleave than phosphonate ester bond in such a hard condition. The preparation of the title compounds **6** can be rationalized in terms of direct reaction of the phosphonates **5a**–**f** with sodium iodide or potassium iodide in dried acetone under nitrogen for 3–14 h (see Table 1). This method provides a simple and efficient procedure for the synthesis of phosphonate derivatives containing sensitive groups to acid, base or water such as carboxylate ester.

All of the title compounds **6** were confirmed by ^{1}H NMR, IR, MS and elementary analysis. In the ^{1}H NMR spectra of **6**: both the protons in the P–C moiety and P–OCH_3 moiety display doublets, which is due to couplings to the phosphorus. The IR spectra of all compounds showed normal stretching absorption bands, indicating the existence of the Ph–H (~2950 cm^{-1}), C=O (~1720 cm^{-1}), C=C (~1620, ~1450 cm^{-1}), P=O (~1260 cm^{-1}), P–O–C (~1050 cm^{-1}) and P–C (~750 cm^{-1}). The EI mass spectra of compound **6a**–**f**