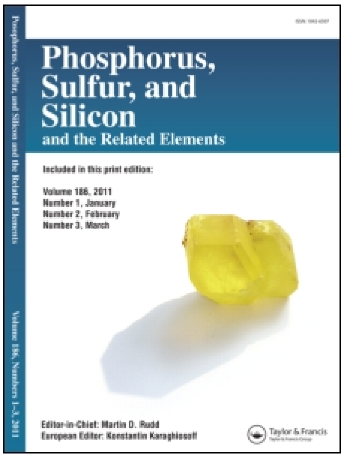

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Synthesis and Dealkylation of 1-(Dichloro-Phenoxyacetoxy)Alkyl Phosphonates

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Using the silylation procedure with chlorotrimethylsilane/sodium iodide followed by alcoholysis, 1-(dichlorophenoxy acetoxy)alkyl phosphonic acid dimethyl esters can be transformed into the parent phosphonic acids without influence on carboxylate ester group.

Keywords: condensation; dealkylation of phosphonates; trimethylsilyl chloride/sodium iodide; phosphonic acid

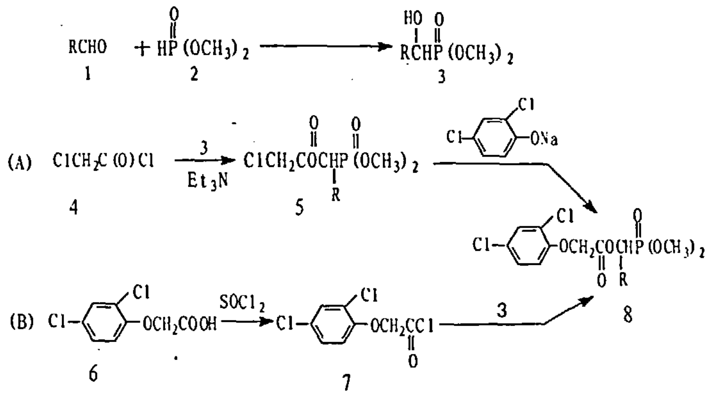
INTRODUCTION

In the course of our research for new phosphonate derivatives with good biological activities, a series of oxophosphonic acid derivatives have been investigated in recent years[1]. Some substituted phenoxy acetoxy alkyl phosphonates have shown herbicidal activities, its corresponding phosphonic acids would be of better biological interest. Therefore, we are interested in extending our investigations to alkyl phosphonic acid with substituted phenoxy acetoxy group such as dichlorophenoxy acetoxy group and finding a mild and efficient method for conversion of dimethyl phosphonate to the corresponding acid.

RESULTS AND DISCUSSIONS

1-(Dichlorophenoxy acetoxy) Alkyl Phosphonic Acid Dimethyl Ester

The following synthetic route A and B can be used to obtain the title compounds 8a-g, respectively.



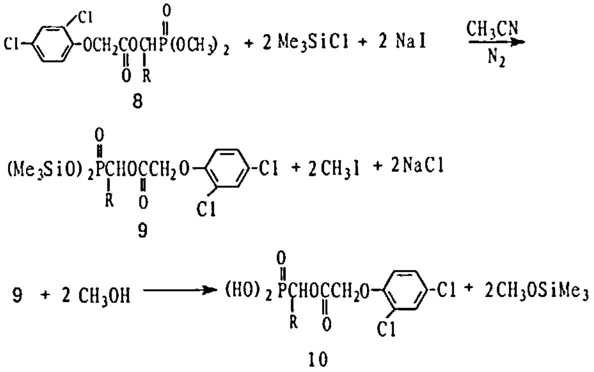
8a~g : R= H, Me, Et, Pr, n-Bu, Ph, o-ClPh

O,O-dimethyl 1- hydroxyalkyl phosphonate 3 can be prepared by addition of dialkyl phosphites to carbonyl compounds using the mixture of potassium fluoride and alumina or Et_3N as catalyst[2]. Compound 3 reacted with chloroacetic chloride in the presence of pyridine to form 1-(chloroacetoxy) alkyl phosphonate 5 in good yield. Thus the title compounds can be synthesized by the reaction of sodium 2,4-dichlorophenoxide with corresponding 1-(chloroacetoxy) alkyl phosphonate in the presence of sodium iodide. This reaction is affected by reaction temperature and solvent, good results can be obtained when the reaction was carried out in polar organic solvent at higher temperature(120 ℃) for 5-6 hrs, the DMF is best choice. At the same time, when synthetic route B was applied, we can choose 2,4-dichlorophenoxy acetic acid 6 as starting material. 2,4-dichlorophenoxy acetic acid 6 is firstly converted to 2,4-dichlorophenoxy acetyl chloride 7 by thionyl chloride, which condensed with dimethyl 1-hydroxy alkyl phosphonates 3 to give the title compound under mild conditions. **8a-d** were obtained in 66.0-75.8% yields by route A and 8e-g in 58.9-63.4% yield by route B. All compounds were identified by ^1H-NMR , IR, elemental analysis and MS .

1-(Dichlorophenoxy Acetoxy) Alkyl Phosphonic Acid

Generally, hydrolysis is the direct means of converting a phosphonic acid ester into the corresponding phosphonic acid[3]. However, this method is not applicable to the phosphonates containing sensitive groups to acid ,base or water such as carboxylate ester. Therefore silylation followed by hydrolysis appears to be the best choice for the preparation of phosphonic acid from corresponding ester. The silylation using trimethylhalosilane has been reported[4,5], bromotrimethylsilane is a highly selective reagent for P-O silyldealkylation of mixed carboxylate-phosphonate alkyl esters[4], but it is expensive.Therefore, we attempted to select chlorotrimethylsilane or chlorotrimethylsilane/sodium iodide as dealkylating reagent.

Our experiments showed the silylation of compounds 8 using chlorotrimethylsilane did not proceed completely at low temperature for long time, however at higher temperature, the carboxylic group was too delicate to survive the harsh reaction conditions. When refluxing compound 8c with chlorotrimethylsilane in acetonitrile at 60 ℃ for 6 hrs, we didn't find the corresponding silyl phosphonate, observing the cleavage of the carboxylate bond in compound 8c instead . Although experiments with chlorotrimethylsilane led to unsatisfactory results,chlorotrimethyl silane/sodium iodide could provide selective dealkylation of phosphonate diesters 8 under mild conditions without influence on carboxylate ester bond. This method involves the treatment of phosphonate diesters with chlorotrimethylsilane/sodium iodide followed by alcoholysis.



10a-g: R= H, Me, Et, Pr, n-Bu, Ph, o-ClPh

Sodium iodide (0.16 mol) in acetonitrile was added to the mixture of phosphonate diesters 8 (0.08 mol) and chlorotrimethylsilane (0.17 mol) in dry acetonitrile below 0 ℃ stirring under nitrogen for 4 hrs and then at room temperature for 3hrs to give the corresponding silylphosphonate 9. Silylphosphonate 9 can be treated directly with alcohol to provide the free phosphonic acids 10, but it was easy to cleave to give 2,4-dichlorophenoxy acetic acid during the hydrolysis procedure with neutral water. The alcoholysis of 9 was carried out with methanol at room temperature for 2hrs and then at 50 ℃ for half an hour to give the phosphonic acid 10a-g . The acids were isolated directly in 75-84 % yields and characterized by IR,^{1}H-NMR, MS.

Acknowledgments

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