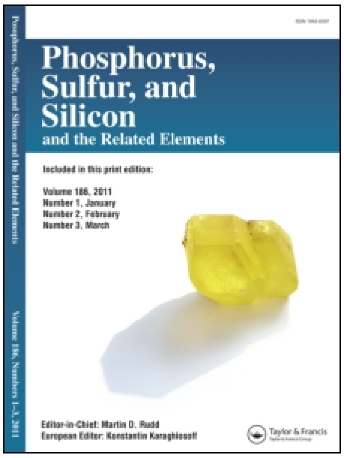

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The Reaction of Phosphoryl Chlorides with Enamines - A New Approach to β-Ketophosphonates

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THE REACTION OF PHOSPHORYL CHLORIDES WITH ENAMINES - A NEW APPROACH TO ß-KETOPHOSPHONATES

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Several approaches are available for the preparation of ß-ketophosphonate esters. A Michaelis-Arbuzov approach using the reaction of an α-halo ketone with a trialkyl phosphite may in certain instances be controlled to favor the preparation of the target materials. However, an alternative pathway leading to the formation of vinyl phosphate esters often predominates. (This reaction system has recently been reviewed by Borowitz and Borowitz.[1]) An alternative approach is that developed in recent years by Wiemer, *et al.*[2] involving the rearrangement of vinyl phosphate esters to the ß-ketophosphonates.

Our laboratory has been interested in exploring additional approaches to this interesting class of compounds. Of particular interest is the reaction involving phosphonylation of enamines, an approach completely analogous to the acylation of enamines for the preparation of ß-diketones[3] and one which does not involve as a reactant the α-haloketone. The current report is an initial presentation of our efforts in the application of this general approach toward the preparation of ß-ketophosphonates.

Enamines derived from the condensation reaction of piperidine with the corresponding ketones were taken in reaction with diethyl phosphorochloridate or diphenyl phosphorochloridate. A three-fold excess of enamine was used in each instance for the formation of the corresponding ß-ketophosphonates.

Reactions were performed using the piperidine enamine derived from four symmetrical ketones: (a) 3-pentanone; (b) cyclopentanone; (c) cyclohexanone; and (d) cycloheptanone. Yields of ß-ketophosphonate products after work-up with aqueous acid were in the range 50-70%. All ß-ketophosphonate products exhibited spectra in accord with their proposed structrues, and single spots on TLC visualized using phosphomolybdate spray reagent. Of particular interest are the IR spectra of these materials which indicate the presence of significant enol content in solution, the amount varying with the structure.

The IR spectra of all products exhibit, in addition to the broadened hydroxyl stretch indicative of hydrogen bonding, a pair of phosphoryl bands resulting from "keto" and "enol" forms of the compounds. The IR bands for the "keto" forms occur at frequencies in accord with that predicted using the correlations of Thomas and Chittenden.[4] At higher frequencies, albeit lower than those predicted[4] for vinylicphosphonate esters, are found the phosphoryl stretching bands corresponding to the intramolecularly hydrogen bonded "enol" forms. Based on intensities of these IR bands, the "enol" forms are more important for the cyclic systems than the open-chain systems, and for the phenyl esters as compared to the ethyl esters.

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