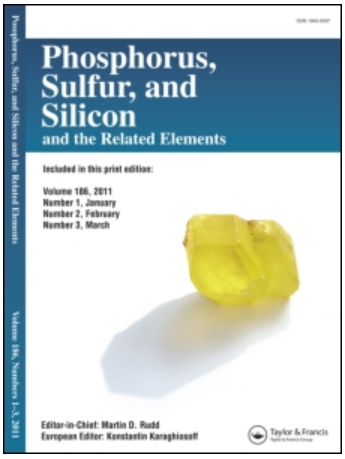

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Use of Pentacovalent Oxaphosphorane Chemistry in the Development of New Methodology for the Synthesis of Natural Products

Cynthia K. McClure[a]; Kang-Yeoun Jung[a]; Christopher Grot[a]
[a] Department of Chemistry and Biochemistry, University of Delaware, Newark, DE, USA

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USE OF PENTACOVALENT OXAPHOSPHORANE CHEMISTRY IN THE DEVELOPMENT OF NEW METHODOLOGY FOR THE SYNTHESIS OF NATURAL PRODUCTS

CYNTHIA K. MCCLURE, KANG-YEOUN JUNG, CHRISTOPHER GROTE
University of Delaware, Department of Chemistry and Biochemistry, Newark, DE 19711 USA

We are presently studying pentacovalent phosphorus chemistry for the design and development of new reagents and methods for organic synthesis. We have found that the condensation reactions between aldehydes and 2,2,2-trialkoxy-1,2-oxaphospholenes, **A1b**, yield β-hydroxy ketones (aldols) that contain an α-methylenephosphonate group in good to fair diastereomeric ratios. The *syn* diastereomer was the major product. This is contrary to the results published by Ramirez using 2,2,2-trialkoxy-1,3,2-dioxaphospholenes, **A1a**, and various carbonyl compounds, where the *anti* isomer was the major product. Use of 2,2,2-trialkoxy-1,3,2-oxazaphospholenes, **A1c**, yields α-amino β-hydroxy carbonyl compounds. Application of this carbonyl condensation reaction to the short and efficient syntheses of *cis*- and *trans*-neocnidilide will be illustrated. Formation of chiral phosphorus in spirophosphoranes by the arresting of pseudorotation around the phosphorus has been accomplished in 1,3,2-dioxaphospholenes with ephedrine as a bidentate ligand (**B1**, **B2**, **B3**). The lack of pseudorotation has been demonstrated by variable temperature NMR studies. All of these results will be presented and discussed.