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

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

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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 -methylene-phosphonate 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 spiraphosphoranes 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.

