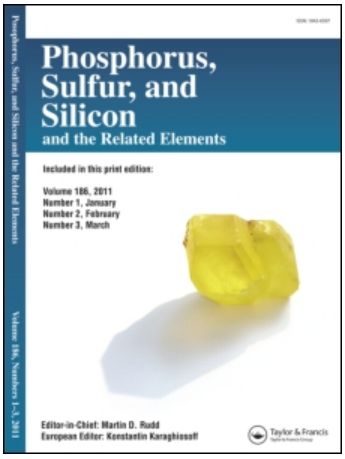

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Synthetic Studies Toward the Preparation of Phosphonate Analogs of Sphingomyelins and Ceramide 1 -Phosphate Using Pentacovalent Organophosphorus Methodology

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SYNTHETIC STUDIES TOWARD THE PREPARATION OF PHOSPHONATE ANALOGS OF SPHINGOMYELINS AND CERAMIDE 1-PHOSPHATE USING PENTACOVALENT ORGANOPHOSPHORUS METHODOLOGY

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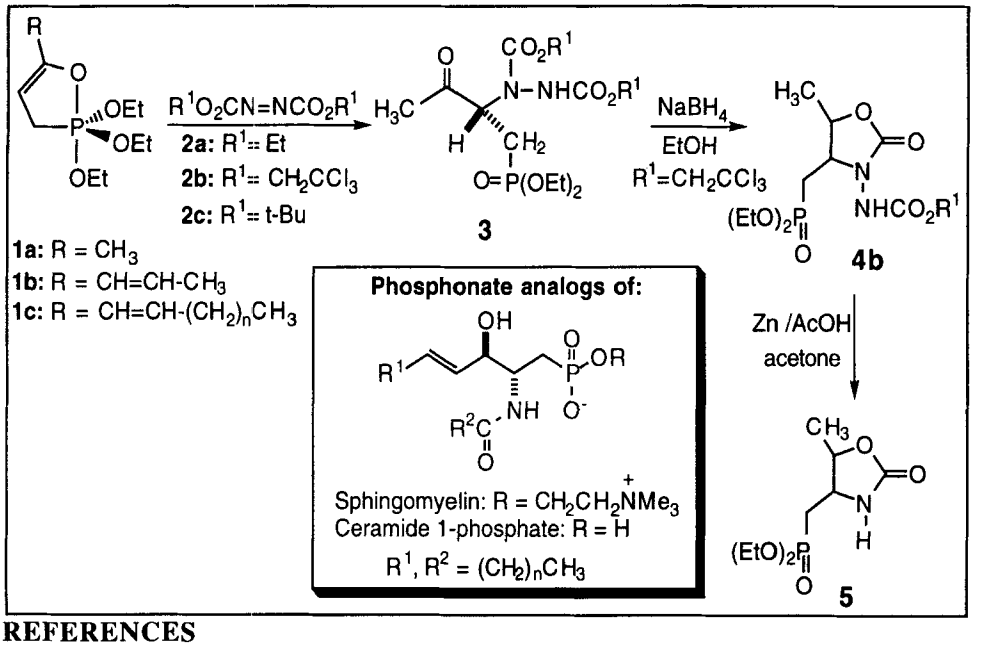
Abstract Non-isosteric phosphonate analogs of sphingomyelin and ceramide 1-phosphate are being synthesized from the condensation product of a pentacovalent oxaphospholene and azodicarboxylates. Model studies are initially described.

Model studies for the syntheses of phosphonate analogs of sphingomyelins and ceramide 1-phosphate are being pursued. The pentacovalent oxaphospholene **1a** readily condenses with dialkyl azodicarboxylates **2a-c** to form the hydrazido-keto-phosphonates **3a-c** in excellent yields.[1] Upon reduction with $NaBH_4$, **3b** produced the oxazolidinone **4b** in high yield (3:1, cis major). Treatment of **4b** with Zn/HOAc/acetone readily cleaved the N-N bond to form **5**. Standard N-N cleavage conditions failed with R = Et, t-Bu. The relative stereochemistry in both diastereomers of **5** was determined by NOE studies. The syntheses of the sphingomyelin and ceramide 1-phosphate derivatives require the use of the P(V) **1c**. We have been successful preparing **1b** from the corresponding dienone. Synthesis of the dienone to form **1c** is being pursued.



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