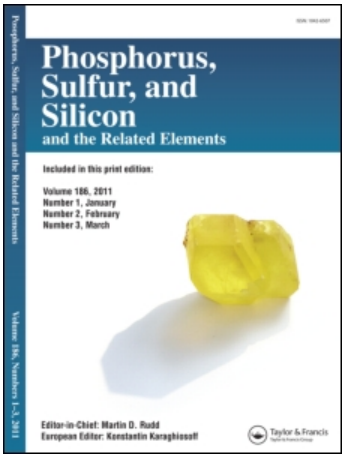

Phosphorus, Sulfur, and Silicon and the Related Elements

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Preparation, Reactions, and Stereochemistry of 4-*Tert*-Butyl-1-Chlorophosphorinane 1-Sulfide and Derivatives

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PREPARATION, REACTIONS, AND STEREOCHEMISTRY OF 4-*TERT*-BUTYL-1-CHLOROPHOSPHORINANE 1-SULFIDE AND DERIVATIVES

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Nucleophilic substitution at tetracoordinated phosphorus centers has been extensively investigated.[1] Transesterification of acyclic phosphinates proceeds with inversion of configuration,[2] whereas four-membered phosphinates react with retention.[3] In previous work[4] we suggested that transesterification in six-membered phosphinates occurs via an S_N2 mechanism. The title compound was synthesized as a model structure to study the stereochemical and mechanistic aspects of nucleophilic substitution at phosphorus in a six-membered ring. A mixture of diastereomers was produced and separated by column chromatography. Both the mixture and separate isomers were used for an investigation of substitution with methanol, methoxide ions, and phenoxide ions; the reactions proceeded with inversion. Transesterification reactions of the resulting thiophosphinates were studied and found to proceed with inversion. Reactions of these with phenyllithium, benzyllithium, lithium phenylacetylide, and the corresponding organomagnesium halides were also carried out. The stereochemical assignments for the title compound (*cis* and *trans*) and two derivatives have been firmly anchored by X-ray studies;[5] assignments for others are tentative and based on spectroscopic measurements, including ^{1}H, ^{13}C, and ^{31}P NMR data.

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