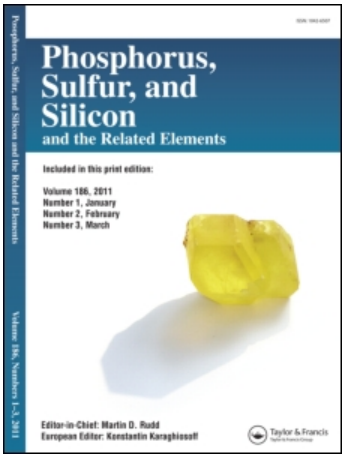

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

The First Example of Optically Active Chlorophosphine: T-Butylphenylphosphinochlorioite

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To cite this Article Omelańczuk, J.(1990) 'The First Example of Optically Active Chlorophosphine: T-Butylphenylphosphinochlorioite', Phosphorus, Sulfur, and Silicon and the Related Elements, 51: 1, 237
To link to this Article: DOI: 10.1080/10426509008040771
URL: http://dx.doi.org/10.1080/10426509008040771

Phosphorus, Sulfur, and Silicon, 1990, Vols. 51/52, p. 237
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THE FIRST EXAMPLE OF OPTICALLY ACTIVE CHLOROPHOSPHINE: t-BUTYLPHENYLPHOSPHINOCHLORIDITE

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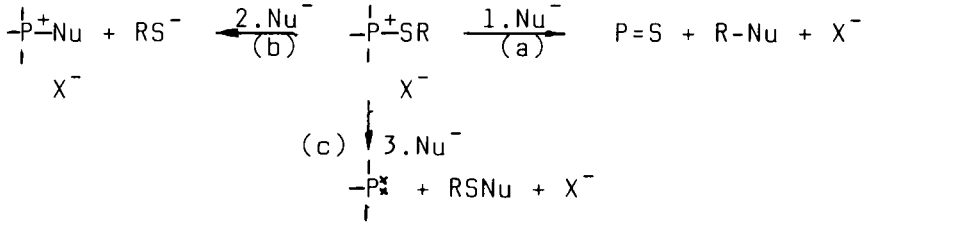
In general, alkylthiophosphonium salts can react with nucleophiles both in the sense of the Arbusov rearrangement (a) and the exchange of alkylthio groups at the P atom (b). We have recently demonstrated[1] that in the case of highly "thiophilic" nucleophiles such as mercaptide anions or tris(N,N-dimethylamine)phosphine the reactive centre is the sulphur atom (c).



The latter reaction (c) has been applied for the highly stereoselective synthesis of optically active phosphines, phosphinous and thiophosphinous acid esters. In continuation of this work we examined the reaction of optically active methylthiochlorophosphonium salts with triphenylphosphine and tris(N,N-dimethylamine)phosphine affording optically active phosphinochloridite. The regioselectivity of this reaction and the stereochemistry of the other halomethylthiophosphonium salts will be discussed in details.

1. J.Omelańczuk, M.Mikołajczyk, J.Am.Chem.Soc., 101, 7292 (1979); J.Omelańczuk, M.Mikołajczyk, Tetrahedron Lett., 25, 2493 (1984).