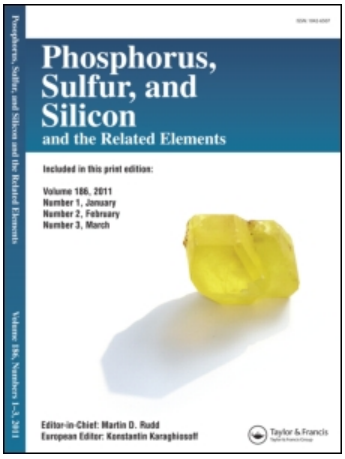

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Synthesis and Characterization of Chiral Dithiophosphate Diesters Based on the Tartrate Backbone; New C_2 Symmetric Chiral Auxiliaries

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SYNTHESIS AND CHARACTERIZATION OF CHIRAL DITHIOPHOSPHATE DIESTERS BASED ON THE TARTRATE BACKBONE; NEW C_2 SYMMETRIC CHIRAL AUXILIARIES

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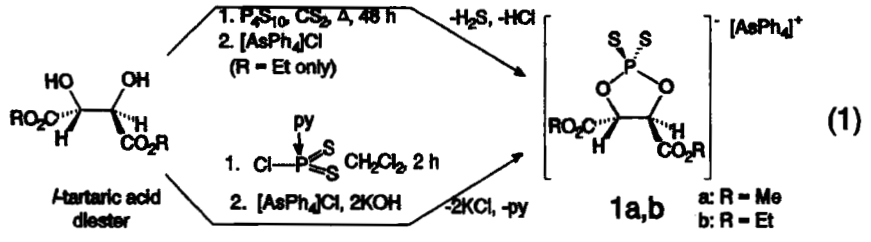
Abstract The reaction of tartaric acid diesters with PS_2Cl•(py) allows for the facile room temperature preparation of new chiral dithiophosphate diesters, one of which has been structurally characterized by single crystal X-ray diffraction.

There is a continuing need for new chiral auxiliaries, especially those with C_2 symmetry,[1] for stoichiometric asymmetric syntheses and enantioselective catalysis. Unfortunately, most C_2 symmetric auxiliaries are either neutral or dianionic, and only a few are monoanions. Even though they would potentially be very useful chiral auxiliaries, few dithiophosphates with C_2 symmetry have been prepared, and only two of their complexes have been crystallographically characterized.[2,3] In this paper we describe: 1) a facile synthesis of new chiral auxiliaries **1** which are based on the derivatives of *l*-tartaric acid; and 2) the structure of one of these, the diethyl ester derivative, **1b**.

Dithiophosphate O,O- diesters are usually prepared by treating phosphorus pentasulfide with an excess of alcohol at elevated temperatures in either neat alcohol or in a high boiling point mixture of alcohol and solvent. When either of these conditions are utilized for the direct reaction of the diesters of *l*-tartaric acid with phosphorus pentasulfide only intractable mixtures result. Phosphorus pentasulfide has limited solubility in hot carbon disulfide and when these solutions are treated with excess diethyl-*l*-tartaric acid for 2 days at reflux it is possible to isolate white crystals as either a lutidinium or tetraphenylarsonium salt of **1b**, equation 1, in excellent yield.



(1)

Unfortunately the conditions in equation 1 are not generalizable to other chiral diols; for example the dimethylester of *l*-tartaric acid requires prolonged periods(> 1 week) at reflux and returns an impure product in low yield. Some time ago, Fluck[4] and Meisel[5] described the preparation of the betaine $PS_2Cl\bullet(py)$ which is readily prepared by treating thiophosphoryl chloride with phosphorus pentasulfide in pyridine at reflux. In subsequent work Meisel has demonstrated the facile reactivity of these complexes with alcohols and amines.[6] When $PS_2Cl\bullet(py)$ is suspended in dichloromethane with a slight excess of diol there is complete conversion to **1a,b** in twenty minutes, equation 1. Important spectroscopic data for **1b** include: NMR(C_6D_6, 22°C) ^1H, 5.05 ppm (d,$^3J_{HP}$ = 6.8 Hz); $^{31}P\{^1H\}$, 131.6 ppm; and IR (KBr), 1760, 1744 cm^{-1}, $\nu(CO_2)_{as}$.

The tetraphenylarsonium salts of **1** readily crystallize from methanol as long colorless needles. These have been characterized by single crystal X-ray diffraction; the *d*-enantiomer of **1b** crystallizes in the chiral monoclinic space group *P2/1* with a = 12.373(2), b = 9.269(2), c = 14.163(3) Å, β = 99.94(3)°, V = 1600(2) Å^3, and R = 7.6%, R_w = 6.7%. An ORTEP view of the anion is shown in Figure 1. Research into the coordination chemistry of these new chiral auxiliaries is currently in progress and will be reported elsewhere.

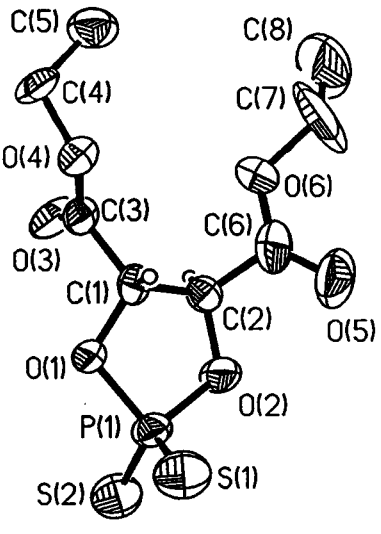


Figure 2 The *d*-enantiomer of **1b**. P-S 1.930(9), P-O 1.34(1) Å, {Average values}, ∠ SPS 120.2(3), ∠ OPO 94.4(6)°.

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6. For example see E. Bauschke, M. Meisel, Phosphorus Sulfur, and Silicon 51/52 372 (1990); and C. Donath, M. Meisel, Ibid page 471.