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The Simple Synthesis of Tetra-Alkyl Sym-Monothiopyrophosphates

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THE SIMPLE SYNTHESIS OF TETRA-ALKYL SYM-MONOTHIOPYROPHOSPHATES

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This poster is a part of our continuing interest in the synthesis and properties of phosphorus acid anhydride analogs, particularly those containing sulfur bridge between two phosphorus atoms (1). Recently we have found that sulfur dichloride reacts with dialkyl trimethylsilyl phosphites 1 to form the tetra-alkyl sym-monothiopyrophosphates 2 in high yield.

$$2 (RO)_2 POSiMe_3 + SCl_2 = \frac{CH_2Cl_2}{-50^{\circ}C} = (RO)_2 \frac{P-S-P(OR)_2 + 2Me_3SiCl_2}{OO}_2 + \frac{1}{2}$$

RO = MeO, EtO,
$$Pr^{i}O$$
, $Bu^{t}CH_{2}O$
(RO)₂ = (CH₃)₂C(CH₂O)₂

Under the reaction conditions no isomerisation of $\underline{2}$ into its asymmetric isomer (RO)₂P(S)-O-P(O)(OR)₂ is observed. The reaction proceeds most probably through the formation of dialkoxy oxophosphoranesulphenyl chloride (RO)₂P(O)SCl. Application of this reaction in nucleotide chemistry will be also mentioned.

 A.Skowrońska, R.Dembiński, R.Kamiński, J.Michalski, J.Chem.Soc., Perkin Trans. I, 1988, 2197.