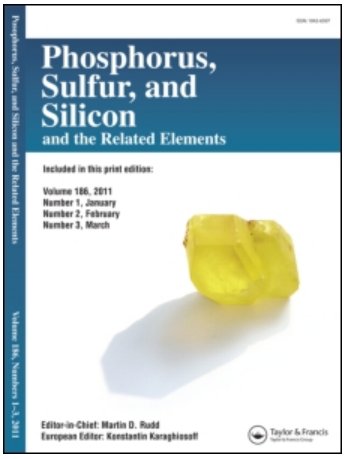

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Synthesis of Pure O,O,S-Trialkyl Phosphorodithioates

P. J. Lake[a]; R. A. G. Marshall[a]
[a] School of Chemistry, Thames Polytechnic, London

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SHORT COMMUNICATION

Synthesis of Pure O,O,S-Trialkyl Phosphorodithioates

P. J. LAKE and R. A. G. MARSHALL

School of Chemistry, Thames Polytechnic, London, SE18 6PF

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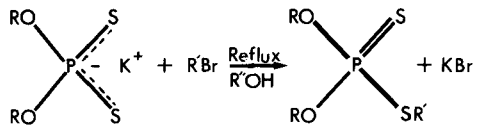
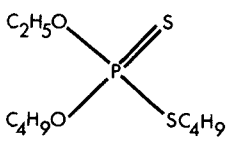
Esters of phosphorodithioic acid are of importance in pesticide formulations[1] and as oil additives.[2] The widely used method of preparation is to reflux the alkali metal salt of dialkyl phosphorodithioic acid with an alkyl bromide in alcoholic solution,[3] i.e.

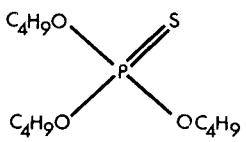


Isobutyl and isopropyl esters have been prepared by refluxing in ethanol solvent for 4–5 h. The ethanol was then removed by distillation under reduced pressure and the product extracted with diethyl ether. This was twice washed with water, dried with magnesium sulphate and the diethyl ether distilled off (typical yield 64%).

The purity of O,O,S-triisobutyl phosphorodithioate was however found by GLC to be only 97%. The principal impurity (2.3%) was identified by GLC/MS as O-ethyl O,S-diisobutyl phosphorodithioate (Structure 1). This was presumed to have arisen from substitution of the isobutyl group in the salt or ester by an ethyl group from the ethanol solvent.[4]



Structure 1



Structure 2

Vacuum distillation at temperatures from 90–95°C (0.1×10^{-3} bar) to 154–156°C (3.3×10^{-3} bar) failed to reduce the concentration of this impurity. It is therefore recommended that the synthesis be carried out in an alcohol solvent with an alkyl group which is the same as that in the phosphorodithioate salt, e.g. isobutanol in this instance. Repetition of the synthesis in this solvent provided a product as expected with a purity of greater than 99%. In addition the yield improved to 80% under identical conditions to those above due probably to the higher reflux temperature in this case (99.5°C, cf. 78.5°C).

A second minor impurity formed whether the solvent was ethanol or isobutanol was O,O,O-triisobutyl phosphorothioate (approx. 0.5%) (Structure 2). This compound probably arises from thermal decomposition of the O,O,S-trialkyl phosphorodithioate itself as it has been shown to be the major product of degradation in pentadecane solution at 220°C.[5]

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