

A Direct Conversion of Carboxylic Acids into Dithioesters

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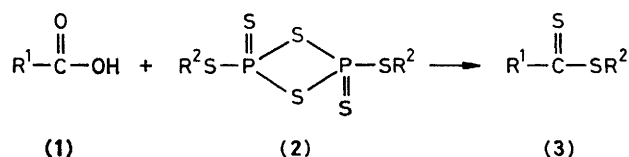
A facile one-pot reaction between carboxylic acids and *S*-alkyl phosphorus sulphides affords the corresponding alkyl dithioesters.

Methods for dithioester synthesis¹ are numerous, but in their technical application they are long, difficult to scale up, or rather expensive. The two that are usually applied use either Grignard reagents and CS₂,^{2,3} or sulphydrolysis of iminothioesters.⁴ Up till now, no one has reported a direct route starting from carboxylic acids. Herein we report a rapid, simple new method starting from readily available and cheap reagents.

The carboxylic acid (1) (2 equiv.) and 2,4-bis(alkylthio)-2,4-dithioxocyclo-di-λ⁶-phosphathiane (2) (1.1 equiv.) in 1,2,4-trichlorobenzene react rapidly in 10 min at 130 °C. The reaction is clean and the dithioester is readily isolated by distillation of the crude mixture. Yields (Table 1) are satisfying for a one-pot reaction.

The overall transformation involves (i) exchange of the hydroxy-group with the alkylthio-group *via* addition of the acid (1) to (2) and cleavage of an intermediate that was monitored by n.m.r. spectroscopy, and (ii) sulphurization of the thioester [R¹-C(=O)-S-R²] by the thioxo moiety.

Carboxylic acid chlorides and anhydrides can also be used but the yields are somewhat lower.



The synthesis of (2) from P₄S₁₀ and MeSH under a controlled pressure has been reported;⁵ the authors assume a monomeric formula, MePS₃ for it, but the mass spectrum makes it clear that the structure is that of the dimer (2).

For the preparation of (2) we used two methods.⁶ The preceding⁵ one was improved by carrying out the reaction in trichlorobenzene at 180 °C, under atmospheric pressure and with a Dewar reflux condenser maintained at -55 °C; the thiol reacts rapidly, H₂S evolves, and the reagent (2) crystallises on cooling.

The reaction of 1 equiv. of P₄S₁₀ with 3 equiv. of MeOH or EtOH in 7 equiv. of trichlorobenzene, affords the *O,O*-dialkyl phosphorodithioic acid; then, as the temperature is raised to about 160 °C, the excess of P₄S₁₀ dissolves rapidly,

Table 1. Preparation of dithioesters^a (3) $R^1-C(=S)-S-R^2$.

R^1	R^2	Solvent	Yield/%
Me	Me	1,2,4-Trichlorobenzene	65
Et	Me	"	62
Pr ⁱ	Me	"	57
Bu ^t	Me	"	57
Me	Et	"	64
Ph	Me	Chlorobenzene	63

^a Identified by their boiling point¹ and n.m.r. spectrum.

insoluble oxygen-phosphorus compounds separate (caution! the reaction is suddenly very exothermic and the solvent boils vigorously); the first intermediate, through a thioxo-mercapto-isomerisation, and reaction with P_4S_{10} gives the reagent (2) in equilibrium with trialkyl phosphorotetrathioate. The clear yellow solution obtained is cooled to 70 °C, decanted, a slight excess of P_4S_{10} is filtered off, and *ca.* 0.5 equiv. of (2) is recovered from the filtrate by further cooling.

This reaction, avoiding the use of obnoxious thiols offers a new and convenient route.⁶

Organophosphorus sulphides, that have been already used with success by Lawesson⁷ for thionation reactions, now allow the simultaneous conversion of hydroxy-groups into alkylthio-groups. The described method is the first reported example of a direct conversion of carboxylic acids into dithioesters and makes easy the preparation of large amounts of alkyl dithio-

esters, which have recently been developed as valuable synthetic intermediates.⁸

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