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Synthesis of sulfines by oxidation of trithioperesters and their rearrangement into acyltrisulfides

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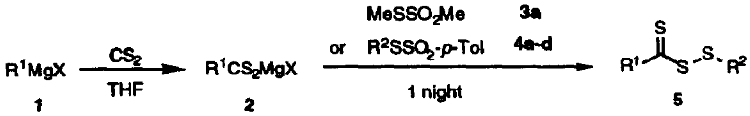
Trithioperesters were synthesised by sulfenylation of halomagnesium alkanedithioates with alkylthiotoluenesulfonates and oxidised by mCPBA. The chemoselective conversion of a thiocarbonyl group into a sulfine moiety was achieved in three cases to yield the first examples of trithioperester sulfines. These compounds undergo at room temperature a novel rearrangement to acyltrisulfides.

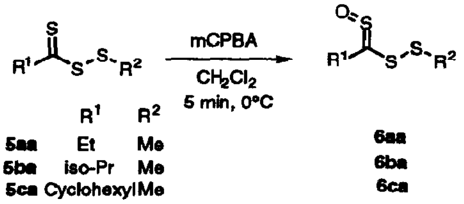
The chemistry of trithioperesters **5** is surprisingly underdeveloped[1-3] despite the pioneering work of Kato *et al.*[1] We wish to report on their conversion into sulfines **6** by oxidation and their subsequent rearrangement into acytrisulfides **8**.

Trithioperesters **5** have been prepared according to Brandsma and co-workers.[3] Reaction of Grignard reagents **1a-d** with carbon disulfide, followed by *in situ* sulfenylation of the resulting dithiocarboxylates **2** with methyl methanethiolsulfonate **3a** led to methyl trithioperesters **5aa**, **5ba**, **5ca** and **5da** in good yields. However this reaction is somewhat limited in scope as only the reagent **3a** is commercially available and expensive, and also, in our hands, tricky to prepare in good yield.[4,5] We had noted in a report[6] that a variety of alkyl *para*-toluenethiolsulfonates **4** are efficient for sulfenylating enolates. In addition their access is straightforward from commercial potassium *para*-toluenesulfonate. Reagents **4a-c** were treated with dithiocarboxylates **2a**, **2b** and **2e** and we were glad to obtain the expected trithioperesters **4** which were isolated after column chromatography with 48-70% yields.[7]



R¹	1	Reagent 3 or 4	R²	5	Yield %
Et	**1a**	**3a**	Me	**5aa**	65
iso-Pr	**1b**	**3a**	Me	**5ba**	56
iso-Pr	**1b**	**4a**	Me	**5ba**	70
iso-Pr	**1b**	**4b**	Et	**5bb**	51
iso-Pr	**1b**	**4c**	CH_2Ph	**5bc**	49
Cyclohexyl	**1c**	**3a**	Me	**5ca**	39
Phenyl	**1d**	**3a**	Me	**5da**	89
para-Tolyl	**1e**	**4b**	Et	**5eb**	48

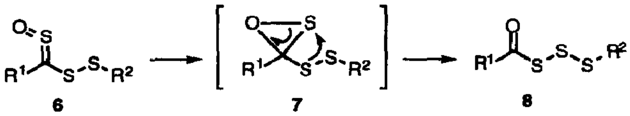
Trithioperesters **5** were treated with one equivalent of *meta*-chloroperoxybenzoic acid (mCPBA). Two sites of oxidation are possible: the thiocarbonyl moiety and the sulfur atom of the alkylthio group. In three cases (**5aa**, **5ba** and **5ca**) we were delighted to observe the chemoselective formation of sulfines **6**, as a mixture of two geometric isomers (*E* and *Z*).[7]



^{13}C NMR signals of the sulfinyl carbon were evidenced for **6ba**: at 200 ppm for the *E* isomer and 204 for the *Z* one. In the proton spectra, the presence of both isomers was revealed by double sets of signals: for instance a methylthio group at 2.4 ppm for the *E* isomer and 2.5 for the *Z* one. Ratios are 70 : 40 (**6aa**), 70 : 30 (**6ba**) and 66 : 33 (**6ca**).

These are the first three examples of trithioperester sulfines, formed by oxidation in an analogous way to that of dithioesters.[8, 9] We have to note that these were formed selectively when the R^2 group is a methyl: apparently only the SMe group is less nucleophilic than the thiocarbonyl. Under similar conditions, the reaction of other trithioperesters (R^2 = Et, CH_2Ph or R^1 = Ph) led to the sulfines **6** but not selectively. Unwanted side products include methyl methanethiosulfonate **3a** (one of our starting materials!), probably arising from a complex pattern of reactivity: oxidation of the alkylthio sulfur, disproportionation to dioxidised species, attack of the trithioperester leading to **3a** and dithioacyl disulfides [products reported by Kato and co-workers[10] to be formed by reaction of dithiocarboxylates with alkanesulfonyl chlorides]. Using dimethyldioxirane as an alternative oxidising agent did not lead to significant change in chemoselectivity.

The thermal stability of sulfines **6ba** and **6ca** were next examined. After 10 days at an ambient temperature a complete conversion into acyltrisulfides **8** was observed. They were characterised by their IR data [νC=O at 1720 cm^{-1} (neat)] and NMR spectra (^{13}C=O at 200 ppm, and proton signal for MeSSSC=O at 2.5 ppm). Acyltrisulfides **8** are compounds reported[11] as early as 1951. They were recently utilized[12] as a source of the trisulfide moiety for onion aroma.



Such a rearrangement is analogous to the novel one we have observed with aliphatic dithioester sulfines.[8,9] It can interpreted through the following pathway: electrocyclisation to an intermediate oxathiirane **7**, opening of this three membered ring with migration of the alkyldithio group to afford acyltrisulfide **8**.

Our results confirm the high reactivity of the thiocarbonyl group against oxidation by a peroxycarboxylic acid.[13] Sulfines of trithioperesters have thus been formed for the first time and their rearrangement to acyltrisulfides has been evidenced, giving thereby a new entry to these molecules.

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