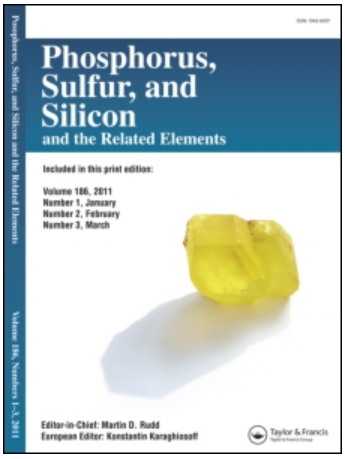

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Reactivity of α,α',-Dioxothiones

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REACTIVITY OF α,α'-DIOXOTHIONES

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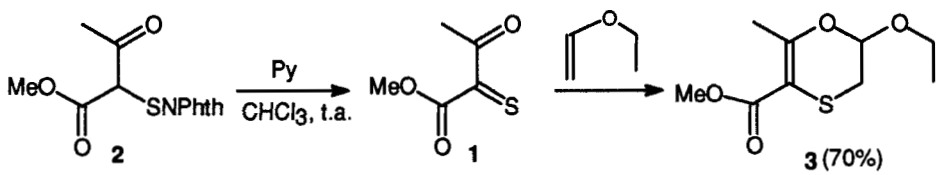
Abstract. α,α'-Dioxothiones obtained from β-ketoesters undergo inverse electron demand Diels-Alder reaction with electron rich alkenes being only the ketonic carbonyl group selectively involved in the cycloaddition. A variety of 1,4-oxathiine derivatives have been prepared following this new type of cycloaddition reaction.

We have previuosly reported as the reaction of phthalimidesulfenyl chloride (PhthNSCl) with ketones as well as with β-diketones and β-ketoesters affords β-oxo and β,β'-dioxothiophtalimides which are precursors of the corresponding α- and α,α'-dioxothiones[1]. Oxothioketones can be generated by action of weak bases and trapped with 1,3-dienes in classical Diels-Alder reaction, affording dihydrothiopyran systems[1].

We have already showed[2] that MeC(O)C(S)C(O)Me can also act as *bis*-heterodiene in inverse electron demand Diels-Alder reactions with electron rich alkenes like enol ethers and related species[2].

We have now investigated the reactivity of thione **1** deriving from β-ketosulfenamide **2**. Treatment of **2** with 2 equivalents of pyridine in chloroform at room temperature, in the presence of ethyl vinyl ether, affords the 3-carbomethoxy substituted oxathiine **3** in 70% yield (Scheme 1).

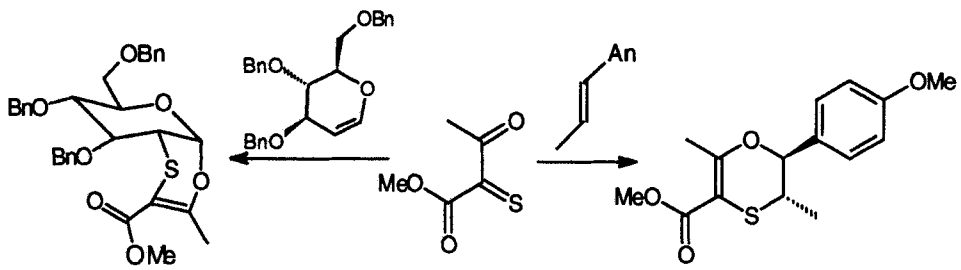


SCHEME 1

Noteworthy this cycloaddition is regio and chemiospecific: the only compound obtained derives from the specific attack of the ketonic oxygen on the hetero-substituted carbon atom of the vinyl ether (Scheme 1).

The use of α-oxothiones deriving from β-ketoesters as versatile diene systems is very general, since the cycloaddition can be carried out with other enol ethers, silyl enol ethers, vinyl sulfides and other electron rich as dienophiles.

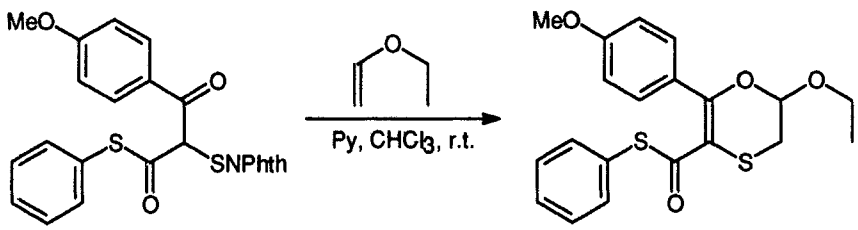
In each case the reaction mantains the characteristic of regio and chemiospecificity. For example when thione **1** was reacted with anethol the stereochemistry of the double bond was retained into the cycloadduct **4** (Scheme 2). Moreover the compound **5** was obtained as single stereoisomer when *tri*-O-benzyl glucal was used as dienophile, opening a new access to thiosugar derivatives (Scheme 2).



5 (38% ; 85% conversion) **4** (50%)

SCHEME 2

The possibility to obtain the cyclodddduct **7** in 87% yield when thiophthalimide **6** was treated with pyridine in the presence of ethyl vinyl ether enlarges the generality of the use of oxothiones as dienes in cycloaddition reactions since β-ketothiolesters are suitable substrates as well (Scheme 3).



6 **7** (87%)

SCHEME 3

The synthesis of α,α'-dioxothiones bearing an optical active group, as well as the trapping of *ortho*-thioquinones following the same strategy, which involves the use of phthalimidesulfenyl chloride, are currently under investigation in our laboratories.

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