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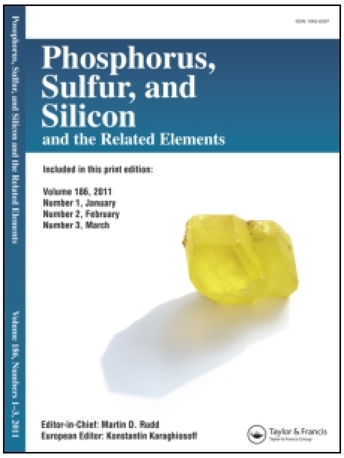

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Synthesis and Isolation of α-Oxo Sulfines

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The synthesis of several α-oxo sulfines is discribed. Various α-oxo sulfines can be isolated as such. The Diels-Alder reaction of these sulfines with 1,3-dienes can be catalyzed by Lewis acids.

KEYWORDS: sulfine, Diels-Alder reaction, Lewis acid catalysis, thiopyran (*S*-oxide)

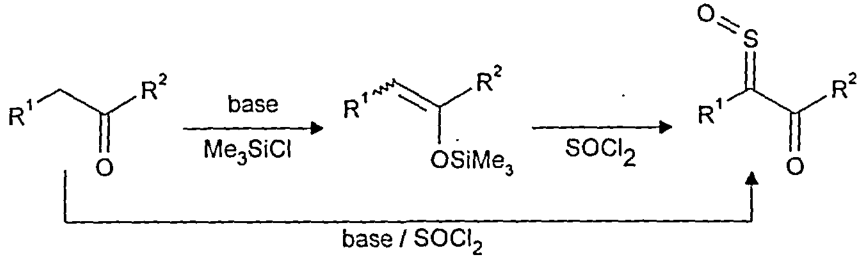
INTRODUCTION

In recent years our efforts in the area of sulfine chemistry[1,2,3] are particularly focused on the synthetic elaboration of α-oxo sulfines.[4,5] This type of sulfines can readily be obtained by reaction of either doubly activated methylene compounds, silyl ketene acetals or silyl enol ethers with thionyl chloride in the presence of a suitable tertiary base. Thus far, α-oxo sulfines have been trapped as their cycloadducts of 1,3-dienes because of their suspected susceptibility toward hydrolysis. However, by a proper modification of the experimental procedures a variety of α-oxo sulfines can be isolated as such. This finding allows a more detailed study of these sulfines with various reagents.

RESULTS

A wide range of differently substituted α-oxo sulfines has been synthesized and isolated in high yields. Representative examples are collected in Table I. The starting compound can either be an ester (entries 1-4), a ketone (entry 5), an aldehyde (entry 6) or a doubly activated methylene compound (entries 7-8). The last mentioned compound is sufficiently enolized to react directly with thionyl chloride in the presence of base to give the α-oxo sulfine. In all other cases, the starting carbonyl compound first had to be converted into the corresponding enol silyl ethers. The thermodynamically more stable geometrical isomer, with the sulfine oxygen *trans* to the carbonyl, was formed exclusively.

TABLE I Synthesis of α-oxo sulfines



entry	R^1	R^2	base	yield (%)[a]
1	Me	OMe	DIPEA	64[b]
2	i-Pr	OMe	DIPEA	89
3	t-Bu	OMe	DIPEA	85
4	Ph	OMe	DIPEA	94
5	Me	Ph	2,6-Lutidine	92
6	$PhCH_2$	H	2,6-Lutidine	80
7	MeOOC	OMe	Et_3N	98
8	NC	OEt	Et_3N	78

[a] yield of crude product unless mentioned otherwise; [b] yield after distillation

The Diels-Alder reaction of α-oxo sulfines with 1,3-dienes conveniently leads to dihydrothiopyran *S*-oxides which are very interesting synthons for the preparation of a wide range of sulfur-containing heterocycles, including thiosugar derivatives. The Diels-Alder reaction of α-oxo sulfines with less reactive 1,3-dienes can be catalyzed by a catalytic amount of tin(IV) chloride. This is the first example of Lewis catalysis in the cycloaddition of sulfines. The synthetic prospects of these cycloadducts are currently under active investigation.

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