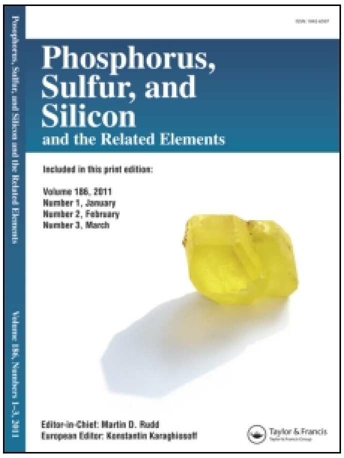

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Thiophilic Addition of Organolithiums to Aliphatic Sulfines
Spontaneous Conversion of Dithioacetal Oxides into Ketones

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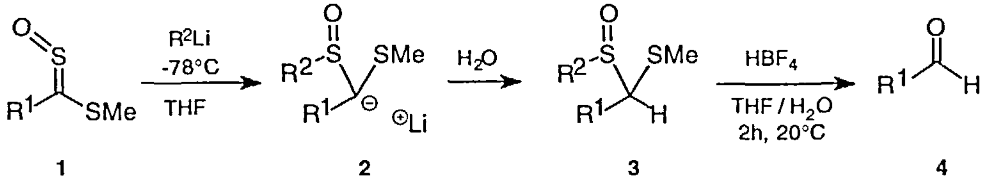
Since the first evidence[1] of a thiophilic addition of organolithiums to sulfines by Schultz and Schlessinger this attractive reaction has received some applications,[2-4] mostly due to the group of Zwanenburg,[2,4] but these are limited to aromatic and non enethiolizable sulfines. Our recent synthesis of aliphatic sulfines[5-7] opened the way to the extension of this reaction. However there was a major concern: competition between addition and deprotonation, as organolithiums are highly basic and the α protons of sulfines have been assumed[8] to be rather acidic.

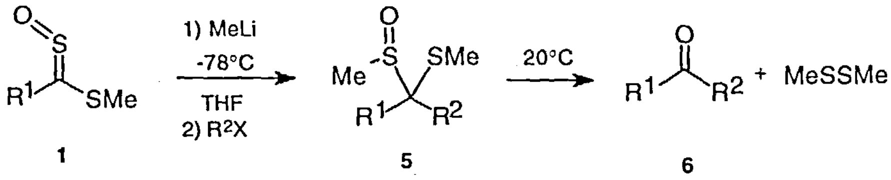
Sulfines **1** were freshly prepared by an oxidation reaction[5,7] of dithioesters with one equivalent of MCPBA. Addition of organolithiums to dithioester S-oxides **1** was examined in THF. Methyllithium and phenyllithium afforded a clean reaction to give, after subsequent addition of water, dithioacetal oxides **3**. Sulfines **1** are extremely electrophilic: the reaction takes place instantaneously at -78°C and can even be carried out at -100°C. Thus a thiophilic addition occurs, demonstrating the electrophilic character of the sulfur atom. No product of carbophilic addition has been detected.



The stereochemistry of the reaction, creating two stereogenic centers, has been approached. The process is not stereospecific, with respect to the configuration of sulfines.

Dithioacetal oxides 3, a masked form of carbonyl compounds, have the advantage over dithianes, as shown by Ogura's group,[9,10] that they are easily converted into aldehydes 4 by simple treatment with a mineral acid.

The intermediates of the thiophilic addition are stabilized carbanions 2 which can be trapped by electrophiles to afford dithioacetal oxides 5. We have observed that these compounds did not even require treatment with a mineral acid to be converted into carbonyl compounds. They readily undergo this transformation at room temperature to ketones 6. This rearrangement, which has few precedents, could involve a sulfoxyde -> sulfenate transposition, subsequent migration of the alkylthio group and elimination of a disulfide.



One advantage of this "*Umpolung*" related chemistry is that it involves an addition reaction instead of a deprotonation. This scheme has been exploited and applied to sulfines bearing a carbonyl group. It provides a new and rapid entry to cyclopentenones *via* intramolecular addition of the intermediate anion.

In conclusion we have shown[11] that aliphatic sulfines undergo selective thiophilic addition with organolithiums, in contrast to the carbophilic addition which takes place with amines.[12] Applications of this reaction are presently investigated.

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