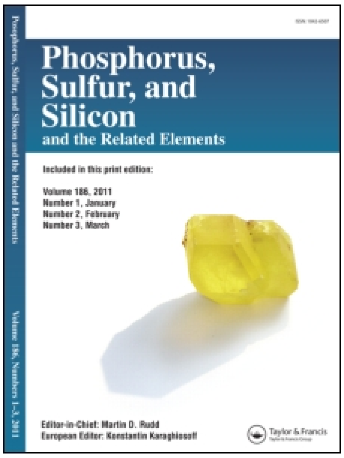

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Sulfines Functionalization with Organosilanes: A Novel Access to Allylsulfoxides

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SULFINES FUNCTIONALIZATION WITH ORGANOSILANES: A NOVEL ACCESS TO ALLYLSULFOXIDES

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Abstract: A novel and general functionalization of sulfines with organosilanes is reported, disclosing a mild methodology to obtain a regiospecific access to a wide range of different substituted sulfoxides.

Thiocarbonyl compounds have gained an increasing interest in organic synthesis, being involved in a large number of chemical transformations.

Our recent interest firstly in the synthesis[1] of thioaldehydes and thioketones and successively in the reactivity of thioketones and dithioesters towards organometallic species, such allylsilanes and benzylsilane,[2] led us to disclose a novel methodology for the synthesis of the corresponding allyl- and benzyl-sulfides, arising from a thiophilic addition of the silylated nucleophile to the carbon-sulfur double bond. These results outlined examples of inversion of the regiochemistry of the attack to the C=S functionality, with respect to the reported lithium and magnesium derivatives, thus showing a new regiochemical control strictly connected to the organometallic species used.

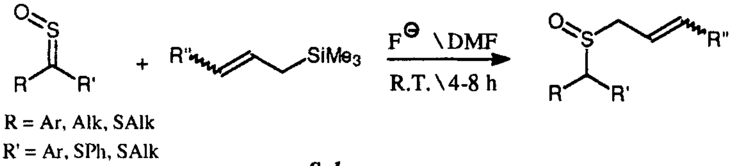
These results prompted us to pursue the investigation to the structurally related S-oxides of thiocarbonyl compounds, namely sulfines, which have been extensively studied by Zwanenburg and co-workers[3] and by other groups[4] and shown to be extremely interesting compounds in a number of synthetically useful reactions.

The reactions of these heterocumulenic compounds with nucleophiles may occur both in a thiophilic or carbophilic fashion, which have been shown dependent on the nature of the nucleophilic agent and of the sulfines used.[3a] Thus while lithium compounds are reported to afford, upon reaction with sulfines, thiophilic addition, amines have been reported to give carbophilic addition.[4a]

To our knowledge, reactions of sulfines with silylated species are still unknown. Our aim was to investigate this kind of reactivity and to study the regiochemical outcome dependance upon the metal species used.

We report in this communication our preliminary results on the fluoride ion induced reactivity of a variety of organosilanes with sulfines.

Thus, for instance, when diarylic sulfines are reacted with allylsilanes, in the presence of anhydrous TBAF as a source of fluoride ion, the corresponding allyl sulfoxides are obtained in good yields (50-73 %) (Scheme).



Scheme

This shows that in the present reaction conditions thiophilic addition is preferred.

Interestingly, this kind of reactivity is not restricted to aromatic sulfines, but can also be conveniently extended to sulfines of different nature, such as sulfines of dithioesters and trithiocarbonates, thus disclosing a novel, mild and general methodology for the regiospecific functionalization of a wide range of sulfines, allowing to isolate again the corresponding allyl sulfoxides.

This reactivity can also be extended to various silylated compounds. In fact, when benzyltrimethylsilane is reacted in the same conditions with the above used sulfines, again a thiophilic addition is evidenced and the corresponding benzyl sulfoxides are isolated in good yields.

So the fluoride ion induced reaction of allylsilanes and benzylsilane can be easily applied to the class of sulfines and it affords a regiospecific and general access to a wide range of benzyl and allyl sulfoxides, useful compounds in organic synthesis, being involved in a large number of stereochemical transformations and asymmetric synthesis.

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