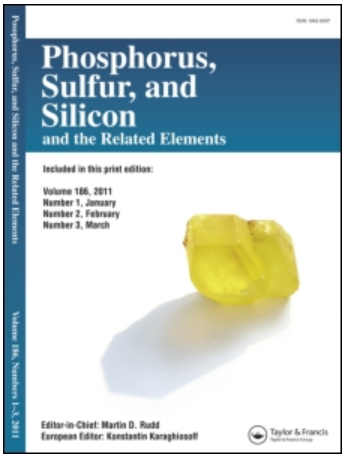

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THIOCARBONYL COMPOUNDS REACTIVITY WITH ORGANOSILANES: FUNCTIONALIZATION WITH α-HETEROSUBSTITUTED SILYL NUCLEOPHILES

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Abstract The reaction of different thioderivatives with several α-heterofunctionalized silyl compounds leads to the products deriving from a regiospecific attack on the sulfur atom of the C=S moiety, affording the corresponding adducts differently functionalized.

The chemistry of thiocarbonyl containing compounds has received an increasing interest in recent years.[1] The reaction of these compounds with various organometallic species, like lithium, sodium or magnesium derivatives has been widely studied.[2]

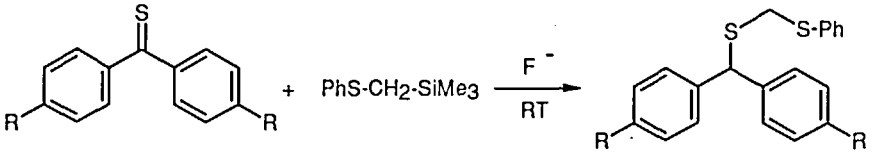
The thiophilic attack is more frequently reported, but other reactional pathways have been observed, such as addition on the carbon atom, reduction, double addition and formation of enesulfides.

Recently we reported[3] that the reaction of different thiocarbonyl compounds with allysilanes and benzylsilane affords adducts deriving from a regiospecific attack on the sulfur atom, showing that with this kind of silylated nucleophiles an inversion of the regiochemistry of the addition on the C=S double bond has been obtained with respect to the already reported reactivity with different organometallic compounds. This kind of reaction has been extended even to the S-oxides analogues of thioderivatives, namely sulfines, and in this case the corresponding allyl- and benzyl sulfoxides, deriving again from a thiophilic attack on the sulfinyl moiety, were isolated.[4]

We report in this communication on the development of such methodology with respect to differently functionalized organosilanes, which should give the obtained molecules a further degree of reactivity. In this context, several α-heterosubstituted silyl compounds have been examined and their behaviour toward different thiocarbonyl containing molecules assessed.

Thus the reaction of aromatic thioketones with (phenylthiomethyl)trimethylsilane, $PhS\text{-}CH_2\text{-}SiMe_3$, in the presence of anhydrous TBAF, afforded the corresponding

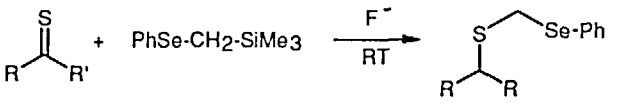
dithioacetal compounds in good yields, thus allowing to obtain polyfunctionalized molecules through a regiospecific thiophilic addition.



R = CH_3, CH_3O

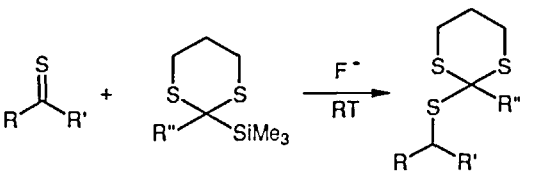
This reaction can be applied to several thiocarbonyl compounds, such as dithioesters and trithiocarbonates and their corresponding sulfines, to afford in the latter case the dithioacetals monoxides in rather good yields.

Interestingly, this reactivity is not limited to sulfur containing organosilanes, but can be efficiently extended to other α-heterosubstituted silyl nucleophiles, like selenoderivatives, to obtain mixed seleno-thio-acetals of thioketones, dithioesters and



trithiocarbonates and of their corresponding sulfines.

When α-difunctionalized silyl compounds have been used, such as 2-trimethylsilyl-1,3-dithiane, we were able to transfer the dithiane moiety onto different thiocarbonyl



containing molecules and to isolate the corresponding adducts, which are now prone to further and interesting functionalizations.

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