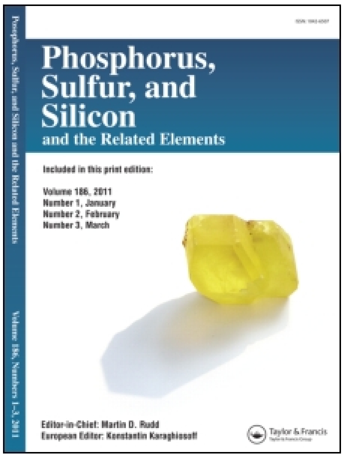

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Fluoride Ion Promoted Reactivity of Thiocarbonyl Containing Molecules with Silyl Derivatives: A Novel Access to Allyl Sulfides

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FLUORIDE ION PROMOTED REACTIVITY OF THIOCARBONYL CONTAINING MOLECULES WITH SILYL DERIVATIVES : A NOVEL ACCESS TO ALLYL SULFIDES

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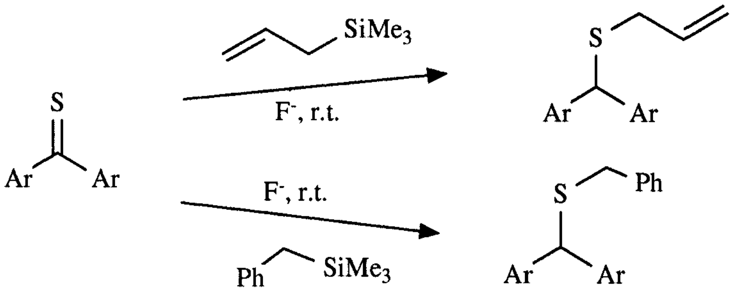
Abstract: Fluoride ion induced reaction of allyl- and benzyl-silanes with thiocarbonyls leads, contrary to the corresponding lithium or Grignard reagents, to products of S-functionalization.

The chemistry of thiocarbonyl containing molecules has seen an increasing interest in the recent years[1]. Moreover, reaction of such compounds with various organometallic species, like lithium, sodium or magnesium halogenides have been extensively studied[2]. Although thiophilic addition is frequently reported, other various reactions can be observed simultaneously, like carbophilic addition, reduction, double addition and formation of enesulfides.

Our recent interest in the development of organosilicon based procedures for the synthesis of sulfur containig compounds[3] led us to investigate the reactivity of thiocarbonyl containing molecules, such as thioketones, dithioesters and trithiocarbonates toward different organometallic species, like derivatives of group 14 elements, namely organosilanes and stannanes.

We report in this communication our findings on the fluoride ion induced reactivity of silylated nucleophiles, such as allylsilanes and benzylsilane toward different thiocarbonyl containing molecules.

Thus, for instance, when reacting different aromatic thioketones either with benzylsilane or allylsilane, a clean reaction occurs, leading in good yields to the corresponding sulfides outlining a clean inversion of the regioselectivity of addition with respect to allyl- and benzyldervatives of lithium and magnesium[2,4].



This reactivity can be conveniently extended to different thiocarbonyl containing molecules, such as dithioesters and trithiocarbonates, in which case again an inversion of regioselectivity is observed, leading to the isolation of S-functionalized products.

Different fluoride ion sources have been tested, like tetrabutylammonium fluoride (TBAF) and tris(dimethylamino)sulfonium difluorotrimethylsilicate (TASF), the former giving generally better yields of the reaction product.

The results obtained then show that the fluoride ion induced reactivity of allylsilanes or benzylsilanes with thioketones and thioesters affords an easy and high yielding access to a wide variety of allylsulfides, otherwise not easily obtainable from the common literature procedures and opens new perspectives in the control of the regiochemistry of such reaction, in strict dependence to the organometallic derivative used.

REFERENCES:

1. E.Vedejs, *Acc. Chem. Res.*, **1984**, *17*, 358.
2. P.Beak, J.Yamamoto, C.J.Upton, *J. Org. Chem.*, **1975**, *40*, 3052; D.Paquer, *Bull. Soc. Chim. Fr.*, **1975**, 1439.
3. A.Capperucci, A.Degl'Innocenti, A.Ricci, A.Mordini, G.Reginato, *J. Org. Chem.*, **1991**, *56*, 7323; G.Capozzi, A.Capperucci, A.Degl'Innocenti, R.Del Duce, S.Menichetti, *Gazz. Chim. Ital.*, **1990**, *120*, 421.
4. V.Rautenstrauch, *Helv. Chim. Acta,* **1974**, *57*, 496; P.Metzener, J.Vialle, A.Vibet, *Tetrahedron*, **1978**, *34*, 2289 and refs. cited therein; S.Masson, M.Saquet, A.Thuillier, *Tetrahedron*, **1977**, *33*, 2949 and refs. cited therein.