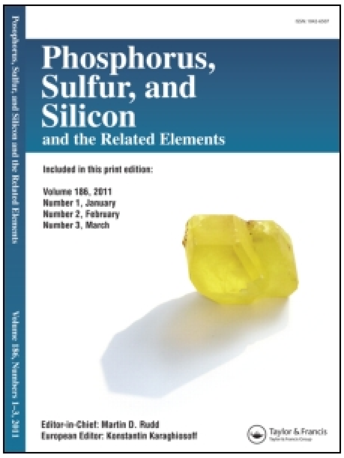

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$CoCl_2.6H_2O$ AND $CF_3SO_3SiMe_3$ INDUCED THIONATION OF ALDEHYDES: A STEREOCONTROLLED ENTRY TO SUBSTITUTED DIHYDROTHIOPYRAN DERIVATIVES.

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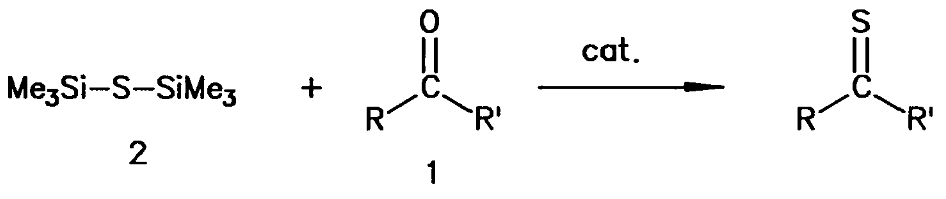
Abstract Bis(trimethylsilyl)sulphide reacts with aldehydes in the presence of a diene under the influence of $CoCl_2.6\ H_2O$ or $CF_3SO_3SiMe_3$ to give the Diels-Alder adducts of the corresponding thioaldehydes. In particular, when using cyclohexadiene, the reaction occurs with a high degree of stereoselectivity and the use of $CF_3SO_3SiMe_3$ allows the stereocontrolled synthesis of both the endo or the exo isomer.

The conversion of a carbonyl function to a thiocarbonyl one has always received considerable attention[1], the thioxo derivatives in synthetic organic chemistry being versatile synthetic intermediates that find many applications in the synthesis of complex natural products[2].

Several methods have so far been reported for the formation of such molecules, based on the direct conversion of carbonyl derivatives, or on pyrolitic and photochemical techniques. While anyway several methods afford the preparation of thioketones, only a very limited number are known to produce "in situ" monomeric thioaldehydes in synthetically useful yields[3], due to the great propensity of these "elusive" compounds to polymerize under the reaction conditions.

We want to report in this communication on a recently developed hexamethyldisilathiane based thionation procedure that affords, under catalytic conditions, the synthesis of thioaldehydes and thioketones in rather mild and convenient conditions. Thus, in fact, upon treatment of an aldehyde or a ketone with hexamethyldisilathiane *(2)* in CH_3CN at room temperature, in the presence of a suitable



R, R'= Me_3Si, H, Alk, Ar, Het.

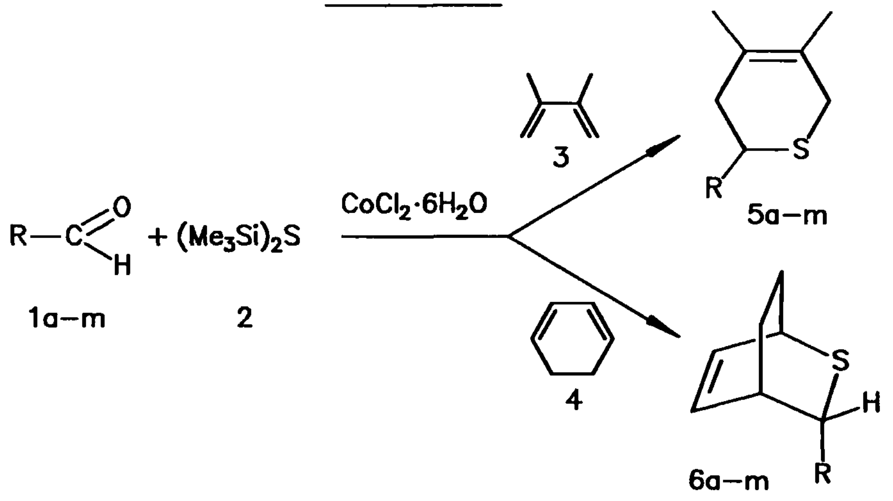
catalyst, the corresponding thioderivatives may be obtained in good to excellent yields.

Several catalytic species have been tested, $CoCl_2.6H_2O$ and $CF_3SO_3SiMe_3$ being the most effective.

The most relevant results have been reported in the Schemes 1 and 2.

$CoCl_2.6H_20$ proved to be an extremely mild and efficient catalyst, affording the

SCHEME 1



R: a=Ph
b=p–$CH_3C_6H_4$
c=p–ClC_6H_4
d=p–BrC_6H_4
e=p–$CHOC_4H_4$
f=2–Furyl
g=2–Thienyl
h=OHC–
i=CH_3CO–
l=PhCO–
m=$PhCH_2OCO$–

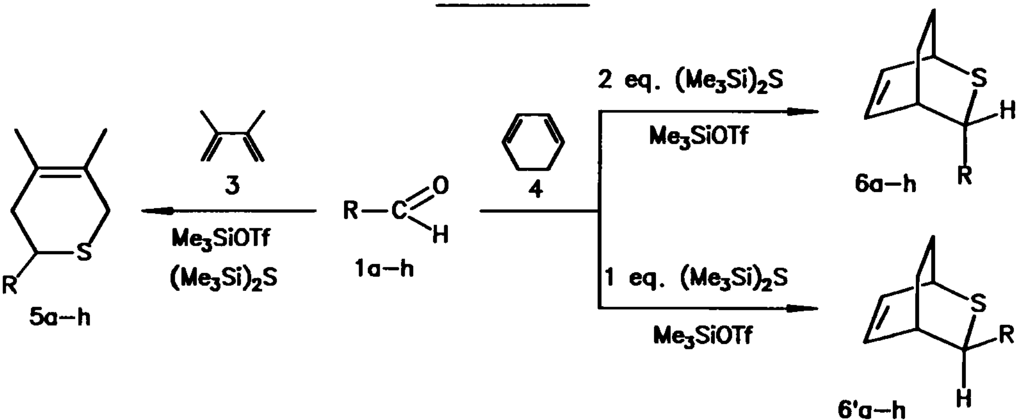
synthesis of silylated thioketones[4,5] and of a wide range of thioaldehydes. While, anyway, thioacylsilanes proved to be rather stable in the reaction medium and could be isolated without difficulties, thioaldehydes, which are known to be rather prone to oligomerization, could be only isolated as dimers and trimers. Nevertheless, the mildness of the method reported allows monomeric thioaldehydes to be efficiently trapped "in situ" by suitable dienes, such as 2,3-dimethyl butadiene *(3)* and cyclohexadiene *(4)*, affording a variety of functionalized dihydrothiopyran systems *(5a-m)* and *(6a-m)*, bearing even very reactive sub stituents, such as the case of *(5h-m)* and *(6h-m)* (Scheme 1).

Not of secondary importance is the fact that this reaction can be performed with excellent yields even in aqueous conditions, as shown by the case of compounds *5h*, *5i* and *5l*, used in their hydrate form or as a 40% solution in water.

Another outstanding feature of this new methodology turned out to be the extremely high chemoselectivity observed, in that it affords the selective thionation of aldehydic functions in the presence of other carbonyl containing functionalities eventually present in the molecule, and its high degree of stereoselectivity, the adduct of the thioaldehydes with cyclohexadiene being obtained usually in over 95% yield of the endo isomer (Scheme 1).

On the other hand, trimethylsilyltriflate proved to possess a wider applicability,

SCHEME 2



R: a=Ph
b=p–$CH_3C_6H_4$
c=p–ClC_6H_4
d=p–BrC_6H_4
e=p–$CHOC_6H_4$
f=2–Furyl
g=2–Thienyl
h=PhCO–

even if a minor degree of selectivity, being able to thionate a large number of ketones, and shows a major interesting feature in its ability to afford selectively the endo *(6a-h)* or the exo *(6'a-h)* isomer of the adduct with cyclohexadiene in strict dependence on the ratio of hexamethyldisilathiane used (Scheme 2). This extremely interesting characteristic allows then an useful stereocontrolled entry into the synthesis of a large number of sulphurated heterocycles.

Thus, in conclusion, while $CoCl_2$ offers an interesting chemoselective and stereoselective thionation of carbonyl compounds, the use of $CF_3SO_3SiMe_3$ allows a stereocontrolled synthesis of both the endo or the exo adduct of the thionated compounds.

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