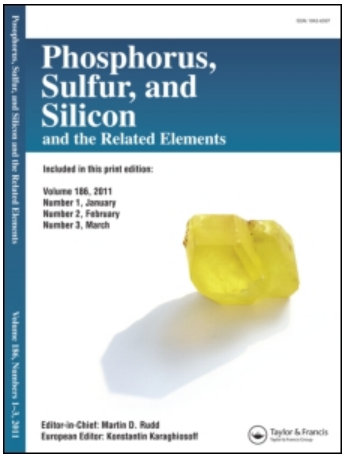

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ORGANOSILANES-MEDIATED SYNTHESIS AND REACTIVITY OF THIOCARBONYL-CONTAINING MOLECULES

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Abstract: The reaction of hexamethyldisilathiane (HMDST) with different carbonyl compounds affords, under the catalysis of $CoCl_2.6H_2O$ or $CF_3SO_3SiMe_3$ a general access to several thioaldehydes and thioketones including acetylenic derivatives and thioformylsilanes. The use of $CF_3SO_3SiMe_3$ allows a stereopredetermined entry to both the *endo* or the *exo* isomers when cyclohexadiene is used as the trapping agent. Furthermore, when using aromatic and heteroaromatic *o*-azidoaldehydes, the reactional behavior of HMDST may well be finely tuned to drive the reaction toward the synthesis of *o*-azidothioaldehydes, fused isothiazole ring systems, aromatic and heteroaromatic *o*-aminoaldehydes and *o*-amino thioaldehydes. Finally, taking advantage of the high reactivity of the C-Si bond under fluoride ion catalysis, a selective regiospecific thiophilic functionalization of thioketones, dithioesters, trithiocarbonates and their sulfines by different organosilanes can be obtained.

Much of the interest in the synthesis and the reactivity of thiocarbonyl compounds relies in the fact that sulfur derivatives in general and in particular compounds containing a thiocarbonyl unit, have gained in recent years an ever increasing importance in synthetic organic chemistry.[1] This was formerly due to their rich and interesting photochemical reactivity,[2] but more recently to the fact that such compounds have been evidenced as key intermediates in the synthesis of complex molecular systems.[3] Thiocarbonyl-containing compounds are in fact able to participate, under mild conditions,[4] to extremely useful chemical transformations, that have recently led to the synthesis of particularly complex natural products, whose family includes molecules with high biological activity and relevant complexity. Such behavior has accentuated the interest in the thiocarbonyl functionality, and put it to the forefront of synthetic organic chemistry, leading to an increasing development of novel synthetic procedures for their preparation and for the exploitation of their synthetic potentialities.

ORGANOSILANES MEDIATED SYNTHESIS OF THIOCARBONYL COMPOUNDS

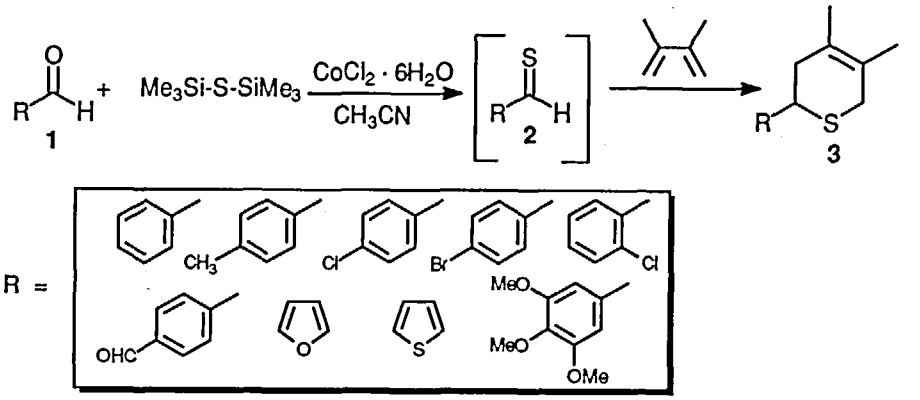
Several methods, ranging from pyrolysis to photochemical techniques, have been reported in the literature for the synthesis of thioketones, direct conversion of carbonyl

units into their corresponding thiocarbonyl analogues remaining anyway the more useful,[5,6] and their chemistry has been extensively studied.[5] In contrast, simple thioaldehydes have historically been considered to be elusive compounds until recently, when Vedejs, through the photochemical cleavage of phenacylsulfides[7] and Krafft,[8] through the fluoride ion induced elimination of α-silyldisulfides, developed synthetically useful methods for their preparations and disclosed their participation in efficient and synthetically useful chemical reactions.

Several other groups have also described Diels-Alder reactions of thioaldehydes generated thermally or by a variety of elimination reactions[9] and, more recently other methods for their preparation have been reported, such as the butyllithium catalyzed conversion of aldehydes with HMDST[10] or the fragmentation of dithiolane S-oxides.[11]

In recent years organosilicon derivatives have played an ever increasing role in synthetic organic chemistry.[12] Much of the logic behind the development of organosilane reagents has relied upon the "proton-silicon correlation". For example, organosilanes undergo a number of thermal rearrangements which phenomenologically have their direct counterparts in analogous proton systems.[13] A number of other processes such as olefin hydrosilylation, carbonyl pseudohalide addition, and silicon transfer to Lewis bases are just a few of the other reactions of silicon for which the proton analogy can be drawn.[14] In this context the synthesis and the reactivity of organosulfur derivatives of silicon have been extensively studied over the years, and they have been evidenced as useful tools in organic synthesis. Following such versatility, a multitude of methods have been developed for their synthesis,[12] and today are rather easily available. These reagents are characterized by the relatively weak silicon-sulfur bond (ca. 70 kcal/mol) which make them good oxigenophiles. In this context, for instance, hexamethyldisilathiane (HMDST) has been reported to convert sulfoxides into sulfides,[15] the driving force for this reaction being the net formation of the Si-O bond.

Starting then from the concept of the proton-silicon correlation coupled with the high reactivity of the sulfur-silicon bond, following the pioneering work of Steliou,[16] we checked the possibility of using hexamethyldisilathiane (HMDST) as a sulfur transfer agent, and we found that the treatment of aldehydes with such compound is of general



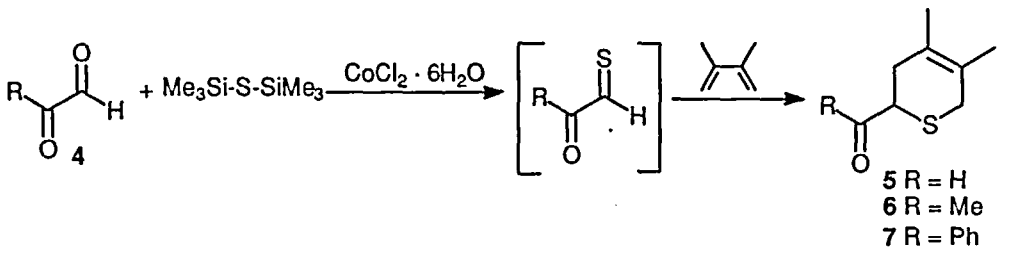
Scheme 1

value for the synthesis of a wide series of thioaldehydes **2**, which can be trapped *in situ* by suitable reagents and that the efficiency of the thionation as well as the stereochemistry of the reaction products are strongly affected by the nature of the catalyst employed.[17]

When aldehydes **1** are treated with bis(trimethylsilyl)sulfide in CH_3CN at room temperature in the presence of catalytic quantities of $CoCl_2.6H_2O$, thioaldehydes **2** are formed efficiently as demonstrated by the high yields of the corresponding cycloadducts **3** obtained by diene trapping, isolated from the reaction mixtures (Scheme 1).

The mild conditions used in the present method minimize deleterious processes, thus permitting thioaldehydes, which are known to be rather prone to polymerization, to exist long enough in the monomeric form to undergo further reactions *in situ*. Thus, on performing the thionation in the presence of dienes such as 2,3-dimethylbutadiene or cyclohexadiene, a variety of functionalized dihydrothiopyran systems are obtained in good to excellent yields starting from a wide range of thioaldehydes. Aromatic aldehydes and aldehydes bearing an electron-withdrawing substituent afford the adducts in high yields, making the bis(trimethylsilyl)sulfide method of thioaldehyde generation comparable to previously reported procedures. On the contrary, most of the trapping reagents employed proved, as expected, to be relatively unreactive with alkanethials, which then participated in alternative undesired reactions.

An interesting aspect of the reaction is its high chemoselectivity which allows selective thionation of aldehydes in the presence of other carbonyl groups. This turns out to be particularly useful when further derivatization of the obtained thiopyrans is required and is of general interest in the thionation of polyfunctionalized aldehydes. Moreover, the reaction is equally efficient with compounds like glioxal, methylglyoxal and phenylglyoxal, which were used as their hydrated or as commercial 40% solution in water (Scheme 2).

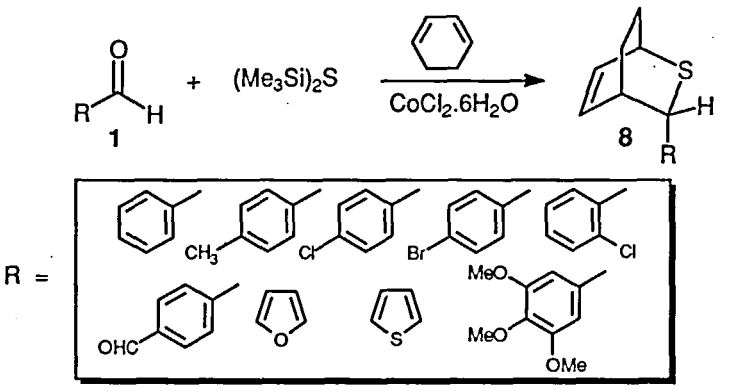


Scheme 2

Even more interesting for exploiting synthetic applications of the thioaldehyde Diels-Alder additions is its stereochemical control of the cyclization step. The reaction of thioaldehydes with cyclohexadiene occurs with very high preference for the formation of the *endo* adduct, with an *endo*/*exo* ratio usually greater than 95 : 5 (Scheme 3).

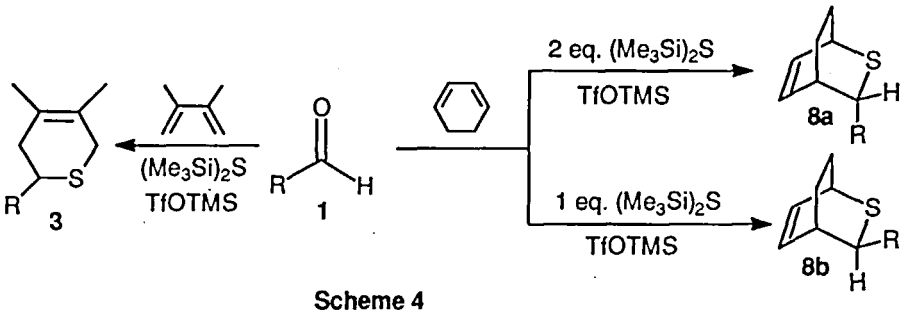
However, following the idea that in the thionation step a suitable activation of the carbonyl function might favor subsequent attack by nucleophiles such as bis(trimethylsilyl)sulfide, the highly oxophilic agent $CF_3SO_3SiMe_3$ was also tried as catalyst for inducing the thionation process. This compound turned out to be effective in

promoting the thionation of the carbonyl compounds, leading to sizeable amounts of the corresponding cycloadducts. Several reactants could be converted to the corresponding thioxo derivatives although only under anhydrous conditions.



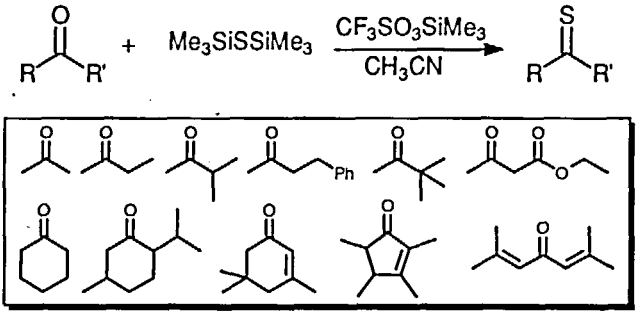
Scheme 3

A unique feature of the use of TfOTMS as catalyst is the stereochemical outcome of the reactions: the Diels-Alder adduct stereochemistry may, in fact, be effectively selected so that the *endo* or the *exo* adduct can be obtained as the predominant diastereoisomer by simply varying the molar ratio of the sulfurating agent. When in fact, a 2 : 1 ratio of $Me_3SiSSiMe_3$ /aldehyde is used, the *endo* isomer is obtained selectively, while on using a 1 : 1 ratio the *exo* isomer is isolated as the predominant isomer (Scheme 4).



Scheme 4

The greater efficiency of TfOTMS in promoting thionation processes with respect to $CoCl_2.6H_2O$ is shown by its ability to induce even the thionation of carbonyl derivatives

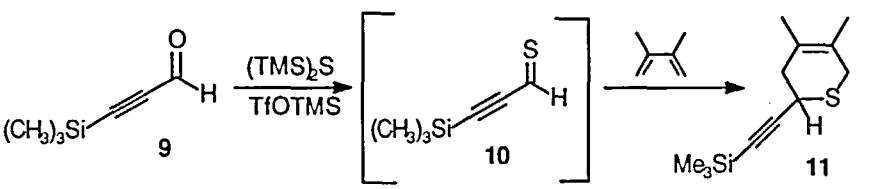


Scheme 5

differing from simple aldehyde such as, for instance, ketones, (Scheme 5).[18] Thioketones, in fact, although more stable than thioaldehydes, show themselves a great tendency to polymerize, unless sterically or electronically stabilized, this demonstrating the still present need to find milder conditions for their generation.

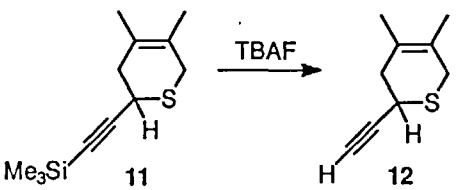
Outstanding features of the $CF_3SO_3SiMe_3$ induced thionathion of ketones are the very mild reactions conditions, which allow the synthesis of a wide range of thioderivatives, and the possibility of minimizing side reactions through a strict control of the stoichiometry of the thionating agent. Acetonitrile proved to be the most efficient solvent, even though the reaction can be equally performed in methylene chloride, albeit with a relevant slowing of the reaction rate. As expected, when thionating the more reactive and less hindered ketones, only their oligomers can be obtained, unless they are trapped *in situ* as the corresponding cycloadducts, while more complex ones can be obtained as monomers. α,β-Unsaturated thioketones may be obtained as well but in this case, as already observed by Metzner and Vialle,[19] the β-position of the enone must be sterically hindered to avoid the formation of the corresponding Michael adduct, thus evidencing a limitation of this methodology.

Following anyway these concepts, several other substrates were tested. One of our most recent results deals in the fact with the first synthesis of an acetylenic thioaldehyde. As mentioned before, such compounds cannot generally be thionated directly, due to competing conjugate additions, and so we thought that a suitably protected compound might as well be as good for the purpose. Thus, on treating the silyl protected propargylaldehyde **9** with HMDST in the presence of TfOTMS a smooth entry into the class of acetylenic thiocarbonyl compounds could be achieved.[20] In this case catalysis of silyl triflate is required, leading $CoCl_2.6H_2O$ to a complex reaction mixture (Scheme 6).



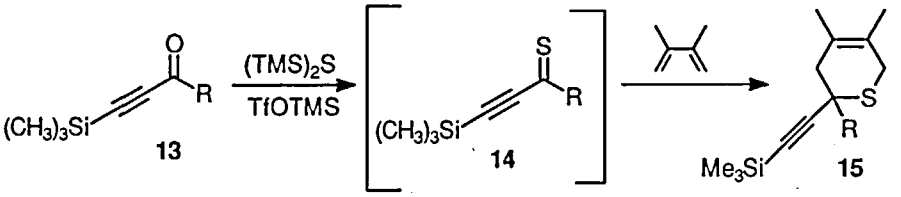
Scheme 6

Then, besides being an helpful tool in the synthesis of thiocarbonyl compounds, silicon proved extremely useful and efficient in protecting position 3 from Michael attack. If necessary, the silicon moiety can easily be removed, under the common desilylation procedures (i.e. TBAF), or, more interestingly, can lead to further elaboration of the acetylenic dihydrothiopyran **12** (Scheme 7).



Scheme 7

This reactivity may well be extended to the synthesis of acetylenic thioketones,[20] which have been efficiently generated and eventually trapped with dimethylbutadiene (Scheme 8). Again, desilylation affords the corresponding unsubstituted acetylenic thioxo compounds. In this context the synthesis of the first acetylenic thioacylsilane has been obtained.

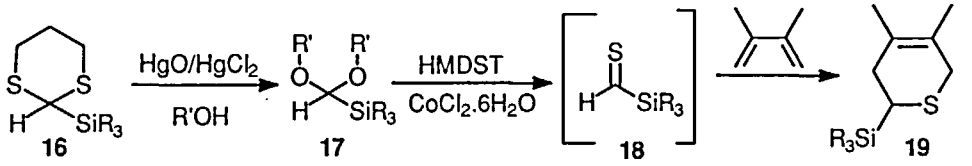


R = $SiMe_3$, CH_3, CH_2CH_2Cl, $C(CH_3)_3$,

Scheme 8

A further example of the versatility, together with the mildness of the methodology, is its application to the synthesis of another class of thiocarbonyl compounds, thioformylsilanes. Such class of compounds should prove extremely interesting in that it conjugates the reactivity of the thiocarbonyl function with the thioacylsilane moiety. Despite anyway the high synthetic potential of these compounds they are still barely explored, and only one example is present in the literature, through the Vedejs' photolytic fragmentation of phenacyl sulfides.[21] Most probably the difficulties in handling formyl silanes,[22] for their very high sensibility to molecular oxygen (*i*-Pr_3SiCHO ignites spontaneously in the air), has hampered up to date a thorough study of their chemistry. Indeed, when we tried to react formyltriisopropylsilane[22] under our conditions, only polymeric material of unknown structure was obtained. A different approach had then to be used and we thought that the silyl acetals **17**, precursors of formylsilanes, could behave as good precursors as well of the wanted thioformylsilanes.

Thus, upon treatment with HMDST of a variety of silylated acetals, easily obtainable through a transacetalization reaction from the corresponding silyl dithianes **16**, the



R = Me, Et, t-Bu, Ph.

Scheme 9

corresponding thioformylsilanes **18** could be obtained in good yields (Scheme 9).[23] This reactivity proved rather general, being compatible with a wide series of substituents on silicon, and allows to point out a novel feature of the HMDST based thionation procedure in its flexibility, demonstrating that, when necessary, different substrates than classical carbonyl compounds can be efficiently employed. This novel synthesis, besides

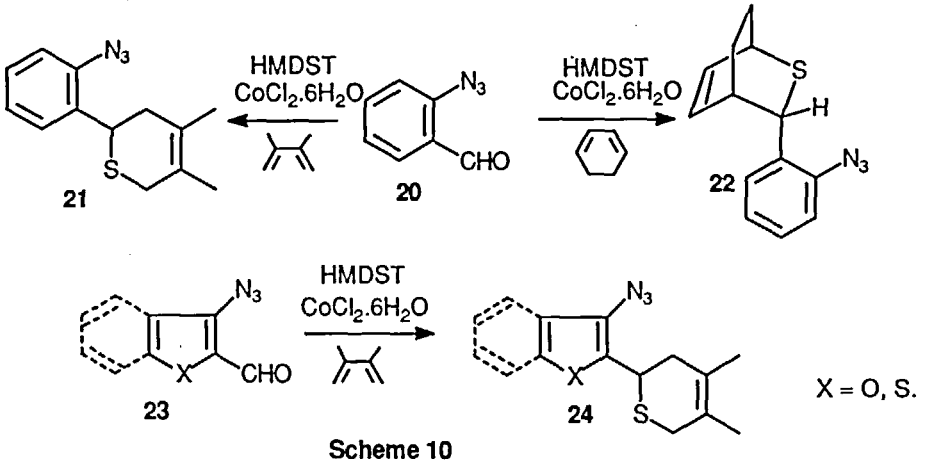
offering a general and mild access to this reactive class of compounds opens the way to a thorough study of their reactional behavior.

FINE TUNING OF HMDST REACTIVITY: THE REACTION OF α-AZIDO ALDEHYDES

Once established the generality and the potentialities of the reported thionation methodology we moved toward different and more intriguing substrates. In connection with other projects being developed in our laboratories, we were attracted by α-azido aldehydes. The presence, in fact, of an azido group could provide an attracting novel site of functionalization for the further synthetic development of such reactive compounds, thus leading to novel applications to organic synthesis. Moreover, due to its intrinsic structure, the azido group might well have been a good trapping agent for the transient thioaldehydes. The thermolysis, in fact, of aryl and heteroarylazides bearing α,β-unsaturated *ortho*-substituents represents a known convenient route to the synthesis of various fused azoles,[24] but only one report is available in the literature concerning intramolecular cyclizations of azides onto an adjacent thiocarbonyl substituent.[25]

In the light of the previous findings, we were therefore prompted to investigate the reaction of *o*-azidobenzaldehyde **20** and several heteroaromatic *o*-azido aldehydes **23** with HMDST in the presence of 2,3-dimethyl-1,3-butadiene and 1,3-cyclohexadiene. Our aim was to uncover whether these dienes might be capable of trapping the thioformyl moiety of the transient thioaldehydes as their Diels-Alder adducts. If this should be the case, concrete evidence should be gained that the synthetic potential of their thioformyl and azido functions might be suitably exploited.

Thus, the reaction of *o*-azidobenzaldehyde **20** in the presence of dimethyl butadiene gave the corresponding thioaldehyde adduct **21** in fairly high yield (Scheme 10).[26] Under similar conditions the heteroaromatic azidoaldehydes **23** also reacted in the presence of the trapping agent to afford functionalized dihydrothiopyrans **24** (Scheme 10). However,



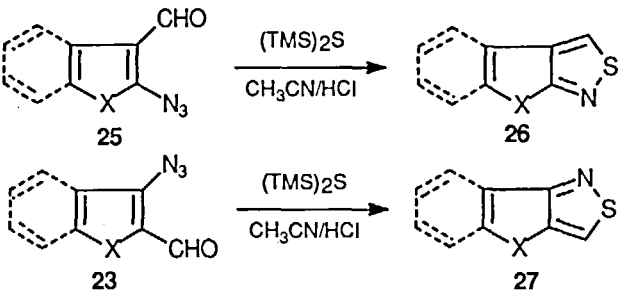
Scheme 10

the mild catalyst $CoCl_2.6H_2O$ was found to be rather ineffective to promote the

thionation of 3-azido-2-formyl benzofuran. In this case a satisfactory yield of the corresponding thiopyran could be obtained by using a stronger Lewis acid such as $CF_3SO_3SiMe_3$, as well as performing the reaction in neat diene.

On the other hand, the reaction proved quite unsuccessful with the 2-azido-3-formyl derivatives, which afforded only unidentified products, probably resulting from ring-cleavage fragmentation of the azido adducts initially formed.

On the other hand, when the same heteroaromatic *o*-azido aldehydes are treated with HMDST this time in the presence of a stronger catalyst such as HCl, the azido group itself can act as efficient thioaldehyde trapping agent, thus offering a novel practicable route to fused isothiazole ring systems (Scheme 11)[27].



Scheme 11

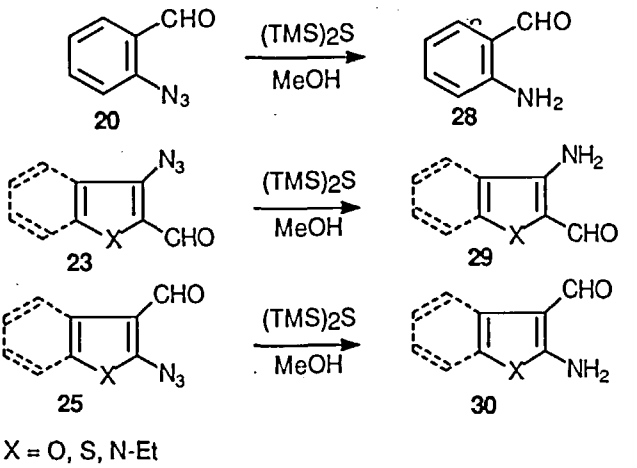
In this case both 3-azido-2-formyl and 2-azido-3-formyl derivatives **23** and **25** may be efficiently reacted affording a selective access to the isomeric benzothieno and benzofuro isothiazoles **26** and **27**. The synthesis of these compounds then is conceivably ascribable to decomposition of the intermediate *o*-azido thioaldehyde, and emphasize the great effectiveness of an heteroaryl azido group to interact with an adjacent thioaldehyde function, resulting in the preferred formation of cyclized isothiazoles even in the case of the α-heteroaryl azides which are known to undergo smooth ring opening upon decomposition.

Differently from the heteroaromatic azides, *o*-azidobenzaldehyde exclusively led to the *o*-azidothiobenzaldehyde trimer, thereby indicating that in such case the intermediate azidothiobenzaldehyde preferred to undergo trimerization reaction rather than intramolecular cyclization to isothiazole. The greater aromatic character of the benzene with respect to the heteroaromatic rings would totally discourage the azide cyclization process in favor of the oligomerization reaction.

Furthermore, on changing the reaction conditions, i.e. on treating the same *o*-azido aldehydes with HMDST this time in methanol, without any added catalyst, a fine tuning of the reactional behavior of HMDST may be achieved, leading this time to selective reduction of the azido function (Scheme 12).[28] This reaction then provide a novel simple and high-yielding procedure for the formation of amines. This method is especially useful for selective reduction of *o*-azido to *o*-amino aldehydes, which are important starting material for the construction of annulated heterocyclic systems, and therefore adds to the one so far employed using gaseous hydrogen sulfide. Moreover, the easy reduction of *o*-

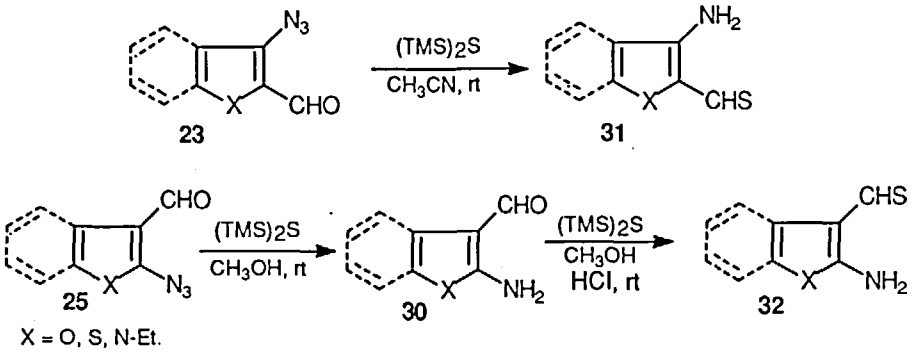
azidoaldehydes, coupled with their observed availability from *o*-nitroaldehydes, furnishes a new convenient entry to *o*-aminoaldehydes from *o*-nitroaldehydes.

In the light of the mentioned results we were subsequently prompted to investigate the



Scheme 12

use of HMDST in the possible direct conversion of *o*-azido aldehydes to *o*-amino thioaldehydes. Thus 3-azido-2-formylfuran in CH_3CN, in the presence of a three-fold excess of HMDST, underwent smooth reaction at room temperature leading to the corresponding amino thioaldehyde through the intermediate aminoaldehyde. Following the same methodology, 3-azido-2-formylbenzo[*b*]furan, 3-azido-2-formylthiophene and 3-azido-2-formylbenzo-[*b*]thiophene were similarly transformed into the respective aminothioaldehydes (Scheme 13).[29] These findings therefore showed that as compared to CH_3OH as solvent, HMDST could perform thionation of the initially formed aminoaldehydes in CH_3CN, evidently suggesting that HMDST can act as a more powerful thionating agent in the latter than in the former solvent. Unlike the isomeric



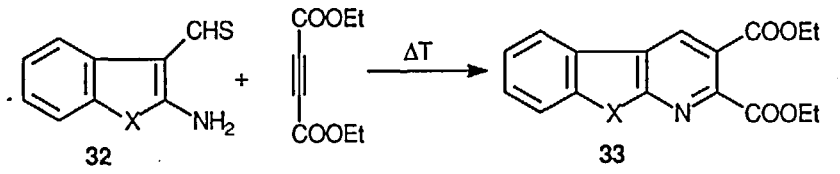
Scheme 13

azido aldehydes, 2-azido-3-formylthiophene, 2-azido-3-formylbenzo[*b*]furan and 2-azido-3-formylbenzo-[*b*]thiophene in neat CH_3CN were only converted by HMDST into their amino derivatives, presumably as a consequence of comparatively lesser reactivity of the formyl moiety in these latter compounds. Upon subsequent addition of HCl the

produced amino aldehydes could actually undergo further reaction with HMDST to give rather complex product mixtures only containing little amounts of the desired aminothioaldehydes. Instead, satisfactory yields of these thioaldehydes were successfully isolated by means of an analogous procedure using CH_3OH solvent instead of CH_3CN.

All the new *o*-amino thioaldehydes are stable orange to red compounds which can be stored in the cold with no significant sign of decomposition. Like the previously reported *o*-aminothioaldehydes in the pyrazole and indole series, the stability of our present thioaldehydes is ascribable to resonance conjugation of the heteroaromatic thioformyl group with the adjacent amino function. In the case of 3-azido-2-thioformylfuran restricted rotation of the thioformyl group was clearly seen from the ^1H NMR spectrum obtained in DMSO which showed the presence of two thioformyl protons in ca. 1 : 1 ratio at δ 10.38 and 10.29 ppm.

Similar to its heterocyclic analogs, *o*-azidobenzaldehyde was readily transformed by HMDST, into *o*-aminothiobenzaldehyde that however proved to be not isolable owing to prompt trimerization (and polymerization) reactions of its thioformyl moiety. As might have been anticipated, in such case aromatic character of the benzene ring would prevent adequate stabilization of the thioformyl function.

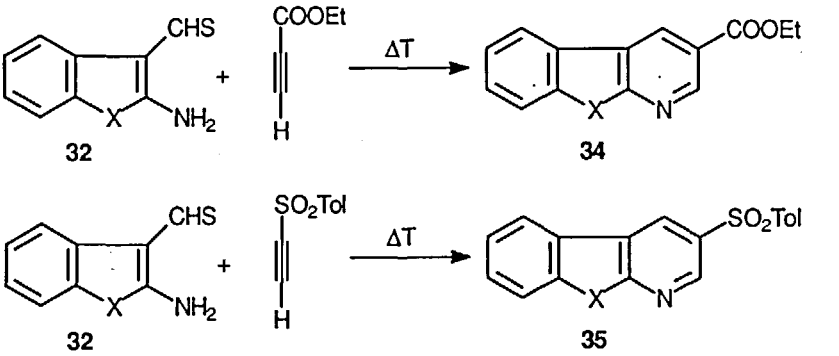


32 33

X = O,S

Scheme 14

Interestingly, the so obtained *o*-aminothioaldehydes may efficiently participate in further reactions, with activated acetylenic derivatives, thus leading to a novel synthesis of *b*-fused pyridine systems. Thus, for example, on reacting 2-amino-3-thioformyl-benzofuran, indole and thiophene with acetylendicarboxylate a smooth entry to the dicarbetoxy derivatives of the parent pyridine fused system may be achieved (Scheme 14).[30]



32 34

32 35

X = O,S.

Scheme 15

This reactivity then offers a novel selective entry to functionalized fused pyridine systems. Interestigly, it affords an additional example of application of such reactive compounds in organic synthesis.

The reactivity is not restricted to acetylen dicarboxylate, but may be conveniently extended to different acetylenic derivatives such acetylene monocarboxylate or ethynyl (*p*-tolyl)sulfone. In these cases only the 3-substituted isomer have been obtained, thus disclosing a regiospecific access to functionalized pyridine ring systems (Scheme 15).[30]

ORGANOSILANES INDUCED REACTIVITY OF THIOCARBONYL COMPOUNDS

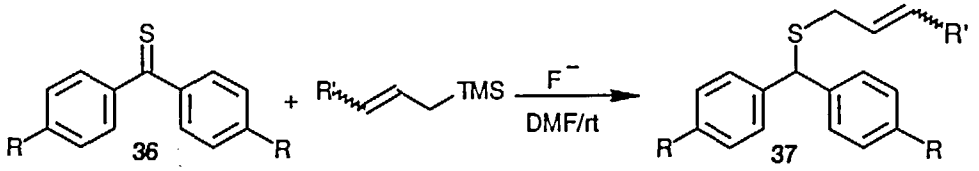
The reaction of organolithium and sodium derivatives and of Grignard reagents with different thiocarbonyl containing compounds is now well documented.[31] Thiophilic addition is frequently reported, thus confirming the prediction of a possible reverse polarity of the thiocarbonyl compared to the carbonyl function. However, other various reactions can be observed simultaneously such as carbophilic addition, reduction, double addition, and formation of enesulfides.

In particular, Beak reported that unsaturated and vinyl lithium and Grignard reagents react with thiocarbonyl compounds exclusively in a thiophilic fashion,[32] while the addition of allylic magnesium halogenides has led to intriguing results. It has been reported that some thioketones react with allylic Grignard reagents affording the product deriving from a direct carbophilic addition in which an allylic shift has occurred.[33] In a similar way dithioesters react with the same reagents with direct carbophilic addition and inversion of the allylic chain.[34]

On the other hand, the formation of C-allylated products without inversion of the allylic chain has been observed in the reaction of adamantanethione with prenyllithium[35] while the reaction of 3,3-dimethyl-2-thioxo ethylbutanoate with butenyl magnesium bromide was rationalized through an initial thiophilic addition followed by a [2,3]-sigmatropic rearrangement.[36]

Although organosilanes have received a great deal of attention in the last decades, due to their great utility in organic synthesis they have never been used in reactions with thiocarbonyl containing molecules.

As a part of our recent involvement in the aforementioned development of organosilicon-based procedures for the synthesis of sulfur containing compounds, we



R = Me, OMe
R' = H, Ph, CHMePh

Scheme 16

have also investigated the reactivity of allylsilanes toward thiocarbonyl derivatives and

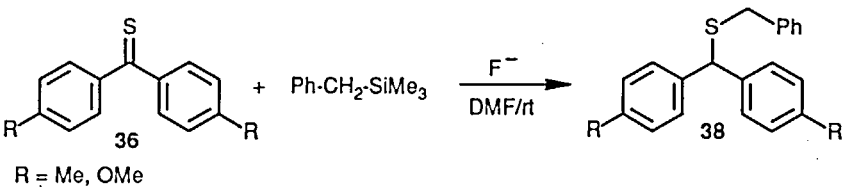
found a novel access to allyl sulfides, through direct exposure of thioketones to allylsilanes under the catalytic influence of fluoride ion (Scheme 16).[37]

Upon reacting different thioketones with a variety of allylsilanes in the presence of TBAF, we were able to isolate from the reaction mixtures only products deriving from a clean thiophilic attack. It is interesting to note that the regiochemical outcome contrasts with what has always been observed in the literature with allylic derivatives.

The reactivity appears to be related to the structure of thiocarbonyl derivatives: while di-*p*-tolylthioketone and thioxanthone afforded good yields of the expected allyl sulfides, thiocamphor proved to be rather unreactive. This result was not unexpected, due to the well known difficulty of this particular thioketone to react in the thiocarbonyl rather than in its enethiol form.

Also the allylsilane structure plays in this reaction a crucial role: allyl shift has not been observed in the reactions with γ-substituted allylsilanes. With these substituted allylsilanes we noticed a slow down of the reaction rate. Nevertheless, the only by-products observed were ketones, arising from decomposition of the starting thiones in reactions which required longer reaction times. Nevertheless, this reactivity, besides offering a new entry into the class of allylsulfides, provides useful means of regiochemical control in strict dependence on the organometallic species used and opens new perspectives in the regioselective functionalization of thioketones.

The observed inversion of regiochemistry seems not to be restricted to allylsilanes, and may be obtained even with benzylsilane, affording in good yields the corresponding benzylsulfides (Scheme 17).[37]

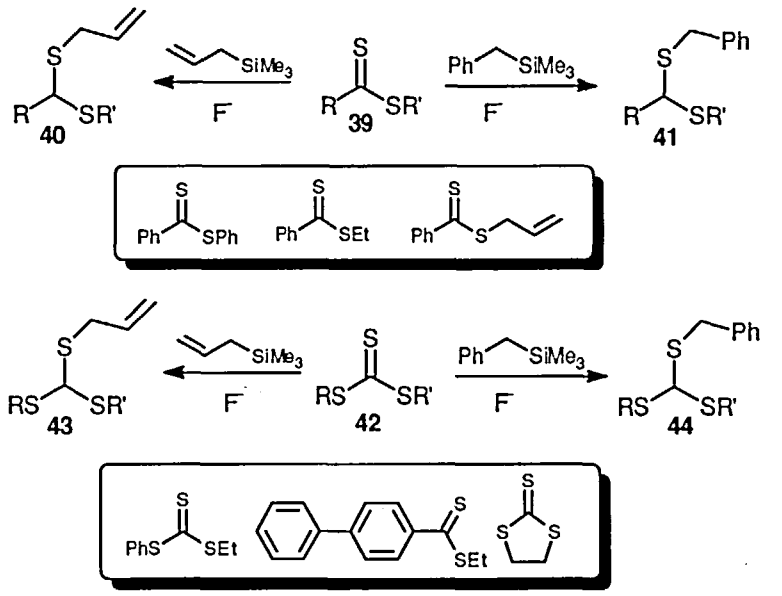


Scheme 17

These reactions may well be extended to other different thiocarbonyl containing compounds such as dithioesters and cyclic or linear trithiocarbonates. Besides confirming the inversion of the regiochemistry, these results outline a completely different reactional pathway to that observed with allylic Grignard reagent, pointing out how the use of organosilanes allows a direct access to allylic and benzylic bis- and tris-sulfides (Scheme 18).[38]

It is interesting to note that products deriving from nucleophilic substitution of R'S-moiety in dithioesters have never been observed.

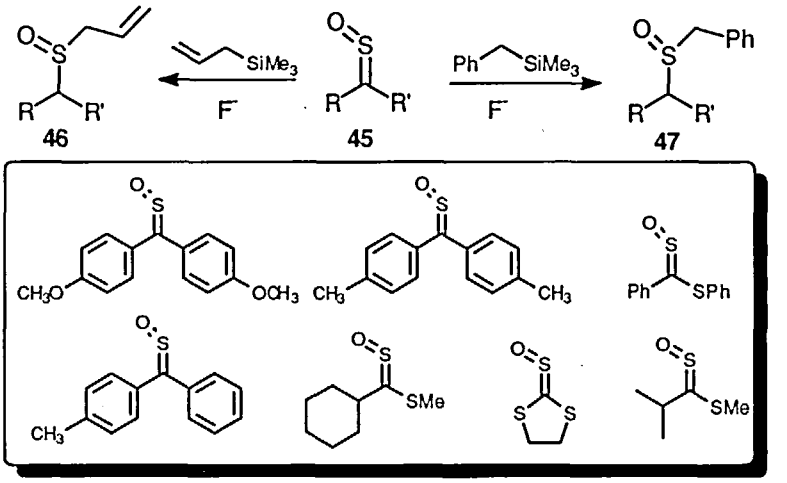
These results show that the actual nature of the starting compounds does not affect this kind of reactivity. Allylsilanes attack from the less hindered site; in fact no product deriving from allyl shift has ever been isolated from the reaction mixtures, even though this possibility cannot be ruled out by using different regioisomeric allylsilanes and also no trace of isomerization of the double bond was observed.



Scheme 18

These results prompted us to pursue the investigation to the structurally related thiocarbonyl S-oxides, namely sulfines, which have been extensively studied by Zwanenburg[39] and by other groups[40] and shown to be extremely interesting compounds in a number of synthetically useful transformations.

The reactions of these heterocumulenic systems 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 sulfine used. Thus, while lithium compounds are reported to afford, upon reaction with sulfines, thiophilic addition, amines have been reported to give carbonyl addition.



Scheme 19

Thus for instance, when diarylic sulfines are reacted with allylsilanes, in the presence of anhydrous TBAF as a source of fluoride ion, the corresponding allylsulfoxides are obtained in good yields. This shows that in the present reaction conditions thiophilic addition is preferred (Scheme 19).[41]

Interestingly, this kind of reaction 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 allylsulfoxides.

Benzylsilane may be used as well, leading to the synthesis of different substituted benzylsulfoxides

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