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Methyl(bismethylthio)sulphonium salts and trimethylsilyl-sulphenyl halides as synthons in organo-sulphur chemistry

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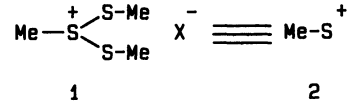
Abstract - Methyl(bismethylthio)sulfonium salts **1** react with nucleophiles like sulphides, alkenes, and alkynes to give respectively methyltiosulphonium, thiiranium, and thiirenium salts. The reaction of **1** with alkenes or alkynes bearing a nucleophilic center in appropriate position gives ring closure with formation of heterocyclic compounds whose nature depend on the position of the nucleophile in the unsaturated hydrocarbons. A new one-pot synthesis of thiiranes from alkenes and trimethylsilylsulphenyl bromide is also described. The timethylsilylsulphenyl bromide is also the key intermediate for a new catalytic desulphurization of thiiranes to alkenes by trimethylsilyl bromide.

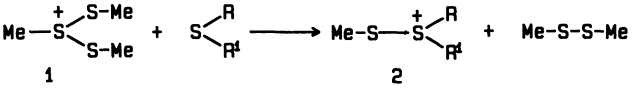
Several years ago we synthesized some methyl(bismethylthio)sulphonium salts **1** and found that they may act as very efficient synthetic equivalents of the methylsulphenylium ion in reactions with nucleophiles of various nature[1,2].



1 **2**

X = $SbCl_6$, BF_4

Scheme I



1 **2**

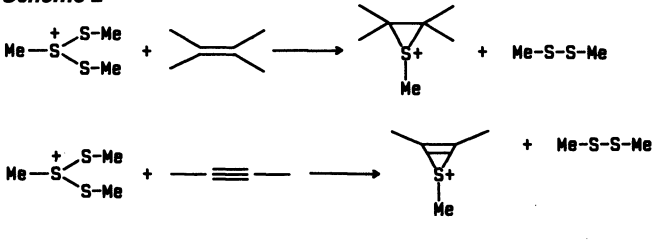
Methyl(bismethylthio)sulphonium hexachloroantimonate reacts[3] with sulphides to give methylthio-substituted sulphonium salts **2** (Scheme 1).

The reactions were carried out with symmetric and asymmetric sulphides as well as with cyclic sulphides. Usually the thio-substituted sulphonium salts are prepared by alkylation of disulphides; however the alkylation of an asymmetric disulphide gives poor regioselectivity and the synthesis of cyclic thio-substituted sulphonium salts is not possible because of the unavailability of the corresponding disulphides. Salts **1** react with alkenes and alkynes in non nucleophilic solvents to give thiiranium and thiirenium salts respectively (Scheme 2)[2,4].

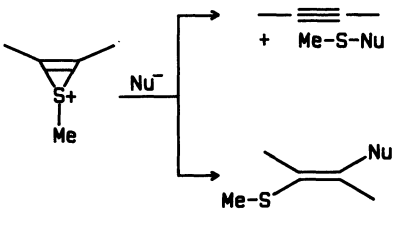
The synthesis of these stable cyclic ions is linked to the absence in solution of strong nucleophiles that usually react with these species. The general reactivity of thiiranium and thiirenium ions with nucleophiles can be due to the attack at sulphur with formation of the unsaturated hydrocarbon or attack at carbon with ring opening of the three membered ring as shown in Scheme 3 for the thiirenium ions.

The two reaction pathwthways depend on the nucleophile even if the attack at sulphur is often masked because of the reversibility of the reaction. This was shown in the reaction of 2,3-di-t-butylthiirenium ion **3** with chloride ion in the presence of 2-butyne. The thiirenium ion **3**

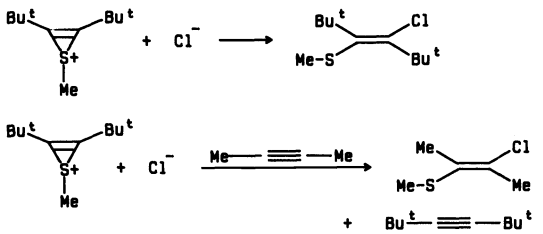
Scheme 2



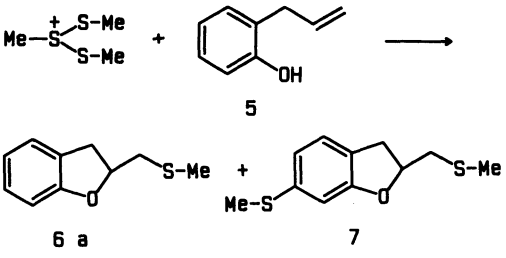
Scheme 3



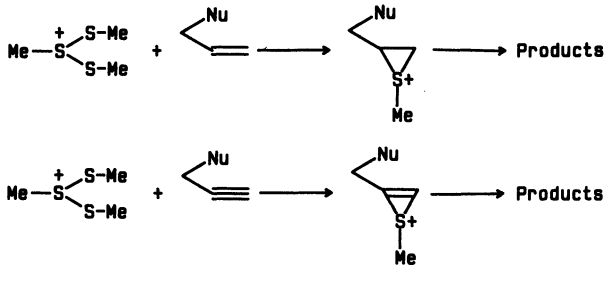
Scheme 4



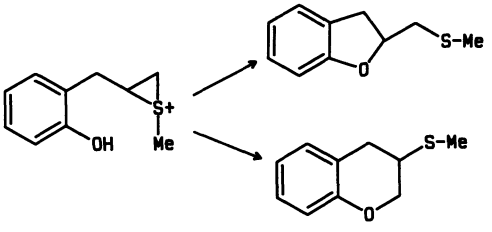
Scheme 7



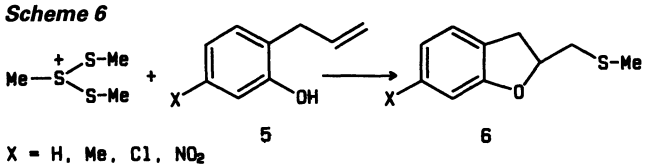
Scheme 5



Scheme 8

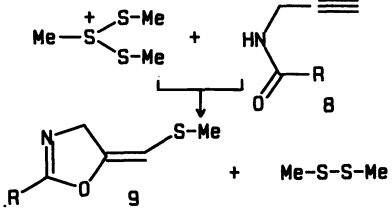


Scheme 6



X = H, Me, Cl, NO_2

Scheme 9



reacts with chloride ion in dichloromethane to give the vinyl chloride **4**. However, when 2-butyne is present in the reaction mixture, the main reaction product is the adduct of methanesulphenyl chloride to this alkyne (Scheme 4). Since the thiirenium ion **3** and 2-butyne do not exchange with the MeS^+ mojety in absence of chloride ion, a reasonable mechanism for this reaction implies the formation in solution of methanesulphenyl chloride which is then trapped by the more reactive alkyne[2].

The easy ring opening of thiiranium and thiirenium ions by nucleophiles suggested to extend the use of methil(bismethylthio)sulphonium ions to the cyclofunctionalization[5] of properly substituted alkenes and alkynes (Scheme 5).

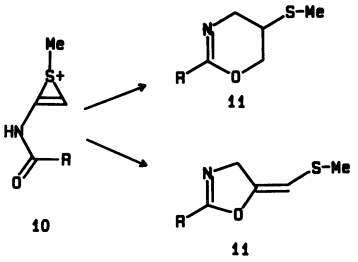
We first applied the cyclofunctionalization with the sulphonium ion **1** to o-allylphenols to obtained methylthio-substituted dihydrobenzofurans **6** (Scheme 6)[6].

In the reaction with the unsubstituted allylphenol we obtained also alkylthiolation at the C-6 of the heterocycle (Scheme 7). The selectivity of the reaction can be controlled by using different reaction conditions. The formation of **7** can be accomplished simply by using a two fold excess of the sulphonium salt. A reasonable selectivity for the synthesis of the dihydrobenzofuran **6a** was obtained running the reaction at -40°.

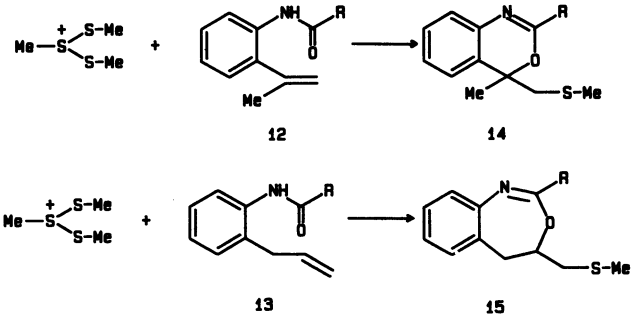
We have suggested for this reaction a mechanism in which the thiiranium ion initially formed undergoes nucleophilic attack by the phenolic oxygen at the internal carbon to give regiospecifically the dihydrobenzofuran ring although the possibility of ring closure to a dihydrobenzopyrane ring also exist (Scheme 8).

The sulphonium salts **1** react also with amidopropynes **8** to give the oxazoline derivatives **9**[7] (Scheme 9).

Scheme 10



Scheme 11



It is reasonable to assume in this reaction that the intermediacy of thiirenium ions **10** allows regiospecific ring closure to the five membered heterocyclic ring. In fact no evidence was obtained for the presence in the reaction mixture of dihydroxaxine derivatives **11** which could also be formed (Scheme 10).

The nucleophilic ring opening of three-membered ring intermediates by the amidic oxygen was further achieved in the cyclofuntionalization of o-vinyl and o-allylbenzamides **12** and **13** with **1** when dihydrobenzoxazines **14** and dihydrobenzoxazepines **15** have been obtained as unique products[8,9] (Scheme 11).

Finally the synthesis of funtionalized indoles **16** and dihydroindoles **17** was obtained from the reaction of **1** with the sulphonamides **18** and **19** respectively[10] (Scheme 12).

In all cases the reaction of ring closure follows the simple roule that the heterocycle formed is only the more favoured according the well known Baldwin's roules[11].

From the data so far reported steams out that the methyl(bismethylthio)-sulphonium ion can be regarded as an usefull synthetic equivalent of a very elusive species,the methylsulphenylium ion.

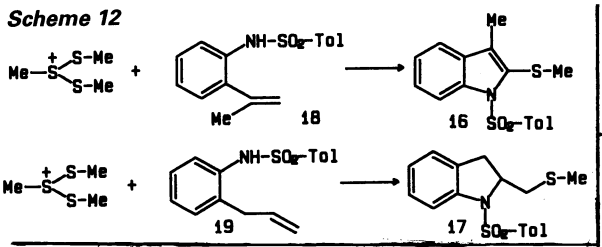
Following our studies, we decided to search for a compound that could behave as synthetic equivalent of a sulphur atom with both nucleophilic and electrophilic properties. We thought that a silyl-substituted sulphenyl halide might be the appropriate species to show this behaviour (Scheme 13). In fact in this derivative the sulphur atom should mantain the electrophilic properties typical of other sulphenic derivatives and the weakness of the silicon-sulphur bond should make the same atom nucleophilic too.

We tried to generate and isolate the silyl-substituted sulphenyl derivative by reaction of bis(trimethylsilyl)sulphide and bromine. However the only products observed at room temperature were trimethylsilyl bromide and sulphur (Scheme 14). We then tried to generate the sulphenyl derivative at low temperature (-78°C) by the same reaction and to trap the intermediate by the addition of an alkene. Following this procedure we were able to obtained the thiirane derivatives as shown in Scheme 15.

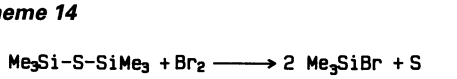
The reaction resulted stereodefensive since the structure of the alkene is retained in the thiirane as demonstrated by the reactions of E and Z 2-hexene which give the trans and cis thiiranes respectively.

We suggest a mechanism in which the sulphenyl bromide formed from bis(trimethylsilyl)sulphide and bromine, reacts with the alkene to give a silyl-substituted thiiranium bromide. Attack of bromide ion at silicon gives the observed product (Scheme 16).

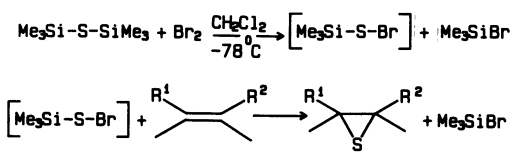
Scheme 12



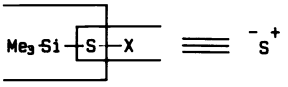
Scheme 14



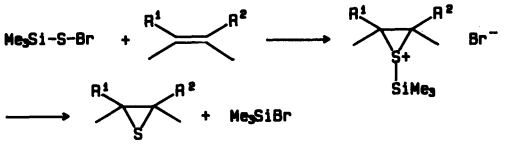
Scheme 15



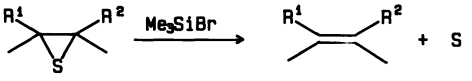
Scheme 13



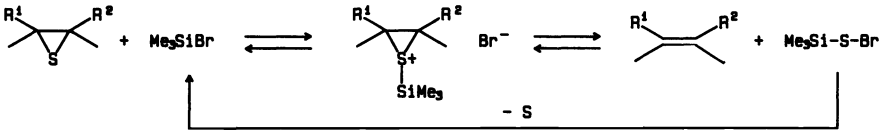
Scheme 16



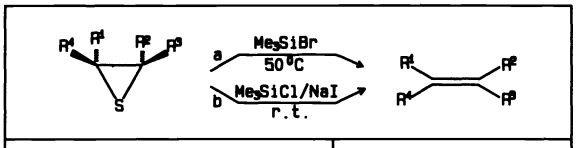
Scheme 17



Scheme 18



Table



R^1	R^2	R^3	R^4	Yield % Method a	Yield % Method b
n-$C_{10}H_{21}$	H	H	H	25	25
C_6H_5	H	C_6H_5	H	40	50
—$(CH_2)_4$—		H	H	40	
—$(CH_2)_6$—		H	H	65	80
C_6H_5	H	H	H	40	
C_6H_5	H	CH_3	H	70	

The main drawback of this one pot synthesis of thiiranes from alkenes is that for the time being it is restricted to 1,2-disubstituted alkenes. The yields are not high and this can be reasonably due to the lability of the trimethylsilylsulphenyl bromide which might have a short life time even at -78°C. Another reason for for the low yields could be the silylation of the thiirane derivatives by the silyl bromide present in solution which might make the reaction reversible.

We tested this reaction in the same conditions used for the synthesis of thiiranes and found that it was not operative. However at higher temperatures we observed desulphurization af thiiranes to alkenes (Scheme 17). Trimethylsilyl iodide also gave desulphurization of thiiranes even at room temperature whereas the corresponding chloride does not react. Better results for this reaction were obtained using sodium iodide in the presence of trimethylsilyl chloride at room temperature. The results obtained for the desulphurization are reported in the Table.

The main feature of this reaction is that it is catalytic with respect to the silyl halide. A possible mechanism implies silylation of the thiirane at sulphur to give the thiiranium halide which can be in equilibrium with the alkene and the silylsulphenyl halide that, in the rection conditions, decomposes to the silyl bromide and sulphur (Scheme 18).

In conclusion we have shown that it is possible to generate at low temperature a silyl-substituted sulphenyl halide that behaves as sulphenylating agent towards alkenes. The chemistry of this new reagent needs a more accurate definition since it might open new ways to introduce a thiol group in an electrophilic way into various organic molecules.

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