SYNTHETIC APPLICATION OF SOME GEMINAL DITHIO-DERIVATIVES

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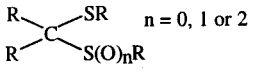
The literature on the preparation and synthetic applications of the mercaptals, α-alkylsulfanyl sulfoxides and α-alkylsulfanyl sulfones is reviewed.

Keywords: mercaptals; sulfoxides; sulfones.

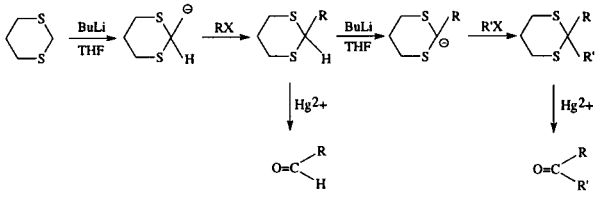
The aim of the present article is to present the literature data on the utilization of some geminal dithio-derivatives for the synthesis of the corresponding carbonyl compounds. Three types of intermediates have been employed, mercaptals n = 0, α-alkylsulfanyl sulfoxides, n = 1 and α-alkylsulfanyl sulfones, n = 2 (Scheme 1). The methods of obtention of each type of derivatives and their transformation into the carbonyl compounds will be presented.



SCHEME 1

MERCAPTALS

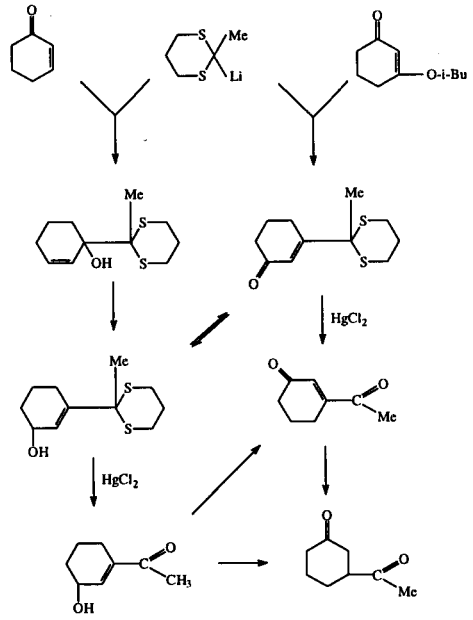
Corey and Seebach[1,2] discovered that dithianes, by treatment with a base, give carbanions, which can easily undergo reactions such alkylation, addition to a carbonyl group and an addition-elimination reaction at an enone center. The substituted dithianes can be converted to the carbonyl compounds by reaction with mercuric chloride. These reactions are exemplified by the syntheses of aliphatic aldehydes and ketones[1,2] (Scheme 2), cyclohexanones[1,3] (Scheme 3) and cyclopentenones[4] (Scheme 4).



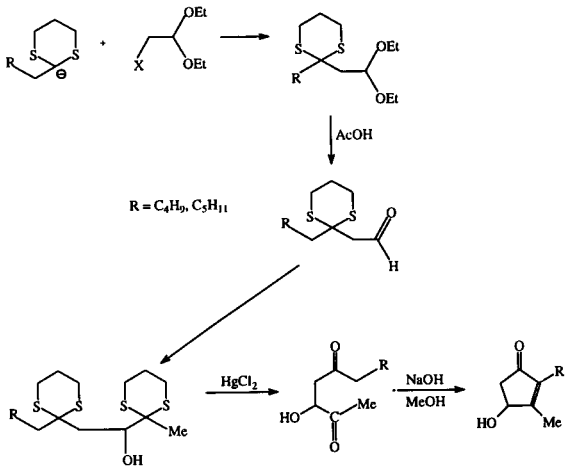
SCHEME 2

In all these reports the dithio-system was derived from formaldehyde, which was transformed to dithiane in order to reverse the polarity of the carbon atom from electrophilic to nucleophilic. However, with the development of sulfanylation reactions it was possible to generate the dithio-system starting from a nucleophilic carbon. This different methodology was employed by Marshall and Roebke[5] for the introduction of a 1,3-dithiano system in the α position to a carbonyl group, using NaH as base and ditosyl sulfide as sulfanylating agent (Scheme 5).

Seebach and al.[6] synthesized the dithio-derivative by a three steps sequence starting from dibromo cyclopropanes. The final hydrolysis was performed using trifluoroacetic acid (Scheme 6).

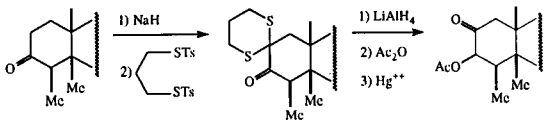


SCHEME 3

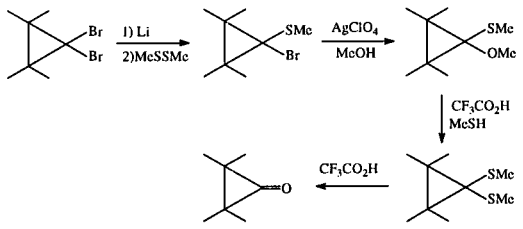


SCHEME 4

Mukaiyama and al.[7] obtained the disulfanylated derivative of a cyclopentanone by reaction of the corresponding enamine with N-phenylthiophtalimide. It is noteworthy that the hydrolysis with

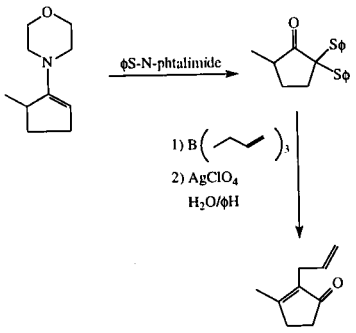


SCHEME 5



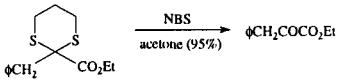
SCHEME 6

silver perchlorate was performed after treatment with triallylborane (Scheme 7).



SCHEME 7

Corey and Erickson[8] reported that 1,3-dithianes, containing in α a keto or carbethoxy groups are resistant to the mercury II reagent, but can be satisfactory converted to the corresponding dicarbonyl compounds by oxidative cleavage using N-bromo or N-chloro succinimide - silver nitrate (Scheme 8).



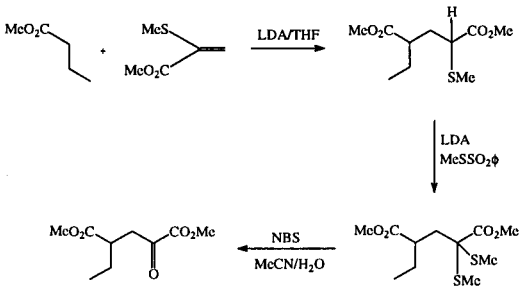
SCHEME 8

Cregge et al.[9] employed also N-bromosuccinimide, in aqueous acetonitrile, for the hydrolysis of some α,α'-dimethylthio-esters. These derivatives were synthesized in two steps: 1) reaction of some nucleophilic species with a Michael acceptor, containing a methylthio group; 2) sulfanylation reaction in order to introduce the second methylthio-group using S-methyl p-toluenethiosulfonate as sulfanylating agent (Schemes 9 and 10).

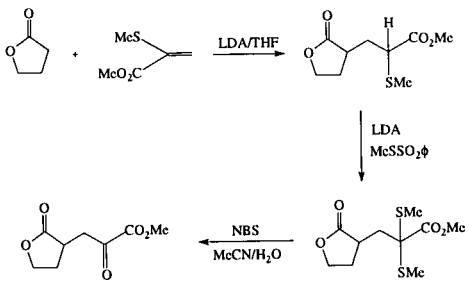
The oxydative hydrolysis of a α,α'-dithio-ester obtained by bisulfanylation of the corresponding ester, was reported by Trost et al.[10] using, instead of NBS, I_2/MeOH, followed by addition of trifluoroacetic acid (Scheme 11).

α-ALKYLSULFANYL SULFOXIDES

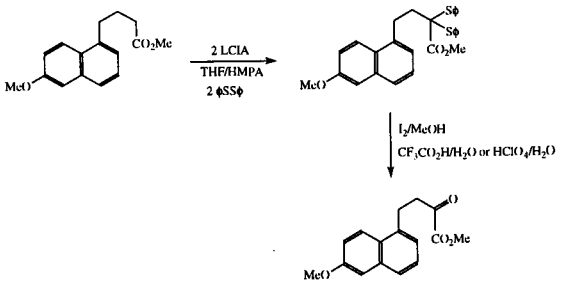
It seems reasonable to suggest that in the oxidative hydrolysis there is an intermediate formation of the α-methylsulfanyl sulfinyl system >C(SMe)(SOMe), which is more easily hydrolysed than the dithio-system.



SCHEME 9

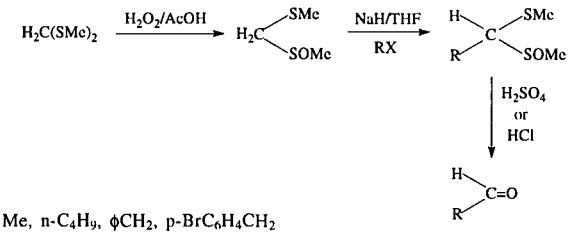


SCHEME 10



SCHEME 11

Ogura and Tsuchihashi[11] reported that the a-methylsulfanyl-sulfoxides are not only easily hydrolysed but that also, due to increase of acidity of the methylene hydrogens, undergo alkylation easily. Thus, a general method for the synthesis of aliphatic aldehydes has been proposed, starting from formaldehyde dimethyl thioacetal, followed by oxidation to monosulfoxide, which would be submitted to alkylation in the presence of base and finally to acid hydrolysis (Scheme 12).

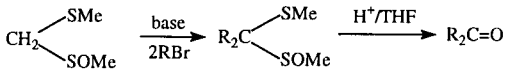


R = Me, n-C_4H_9, ϕCH_2, p-$BrC_6H_4CH_2$

SCHEME 12

The same methodology was employed by Schill and Jones[12] for the synthesis of aliphatic ketones (Scheme 13).

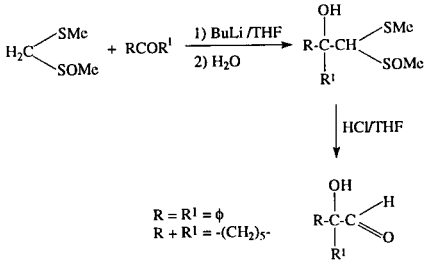
Ogura et al.[13,14] reported two different procedures for the synthesis of hydroxy aldehydes: 1) addition of the carbanion of α-methylsulfanyl-sulfoxide to the carbonyl group of some ketones, followed by acid hydrolysis (Scheme 14); 2) reaction of α-methylsulfanyl-sulfoxide carbanion with esters to give the



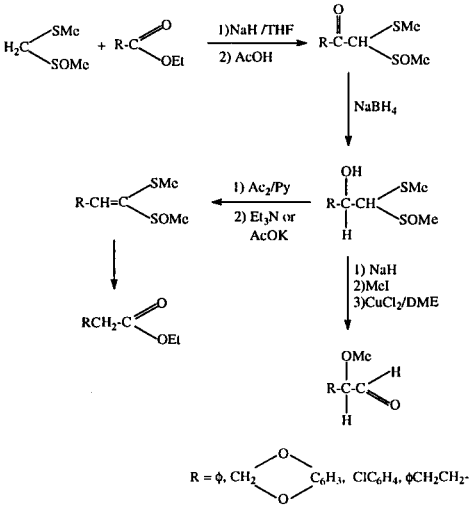
R=n-C_6H_{13}, n-C_8H_{17}, n-$C_{10}H_{21}$, HO-$(CH_2)_{11}$ and n-$C_{12}H_{25}$

SCHEME 13

corresponding α-keto-sulfoxides, followed by reduction to the corresponding α-hydroxy-sulfoxides, and finally by acid hydrolysis (Scheme 15).

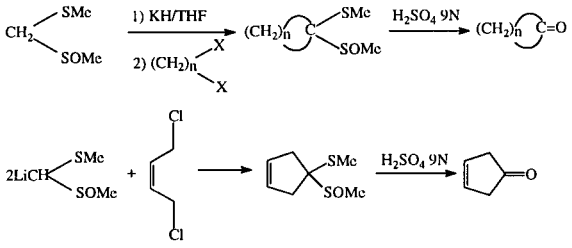


SCHEME 14



SCHEME 15

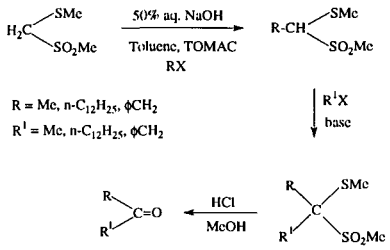
α-Methylsulfanyl-sulfoxides showed to be also useful intermediates for the synthesis of cyclic ketones[15] (Scheme 16).



SCHEME 16

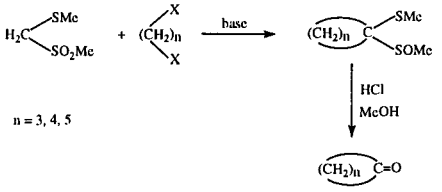
α-ALKYLSULFANYL SULFONES

Ogura et al.[16] reported that α-methylsulfanyl dimethyl sulfone, which is the further oxidation product of formaldehyde dithioacetal, can be more easily alkylated and hydrolysed to afford carbonyl compounds (Scheme 17).



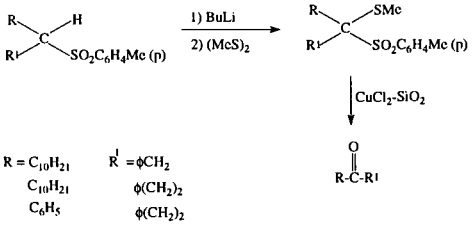
SCHEME 17

Using ω,ω'-dibromides Ogura et al.[16] were able also to obtain some cyclanones (Scheme 18).



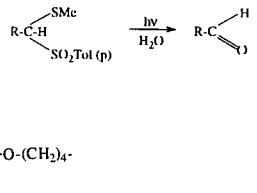
SCHEME 18

Kotaka et al.[17] reported the hydrolysis of dialkyl or alkylphenyl α-methylsulfanyl sulfones to the corresponding dialkyl ketones using $CuCl_2$-SiO_2. It is noteworthy that the intermediate methylthio sulfones were obtained by sulfanylation reaction of α,α'-dialkyl tolyl sulfones employing BuLi and dimethyl disulfide (Scheme 19).



SCHEME 19

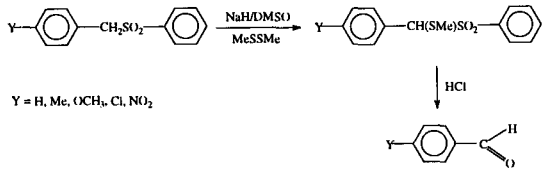
Ogura et al.[18] verified that the α-methylsulfanyl methyl p-tolyl sulfones, mono and di-alkylated may undergo hydrolysis to yield the corresponding aldehydes and ketones by photochemical decomposition (Scheme 20). It is noteworthy that the aldehydes could not be obtained by acid hydrolysis.



R^1 = $C_{12}H_{25}$ R^2 = Me
R^1 + R^2 = -$(CH_2)_5$-

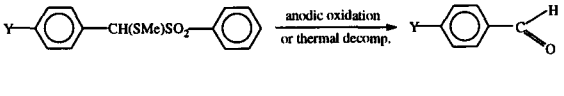
SCHEME 20

In the course of our investigations on the sulfanylation of sulfoxides and sulfones we verified[19] that some benzyl phenyl sulfones afforded α-monosulfanylated derivatives by reaction with dimethyl disulfide in the presence of NaH/DMSO. These derivatives, when submitted to acid hydrolysis, yielded benzaldehydes in 85-95% yield (Scheme 21).



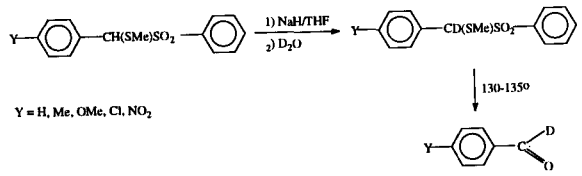
SCHEME 21

However, we were interested in establishing a method of cleavage of these derivatives in non acid conditions, which would be convenient for molecules containing an acid sensitive group. One such method proved to be anodic oxidation.[19] Thus, the electrolyses of these derivatives on platinum electrodes, at constant potential of 2.60V in aqueous acetonitrile containing sodium perchlorate, afforded benzaldehydes in ca. 70-78% yield. Another method[20] was the thermal decomposition which occurred when the α-methylsulfanyl benzylic sulfones were heated at their melting points (130-175°C) to yield benzaldehydes in 70-84% yield (Scheme 22). This procedure has the advantage over the previous one as the aldehydes, mostly liquids, are removed by distillation as soon as they are formed, without any work-up.



SCHEME 22

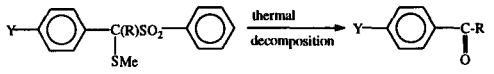
The presence of a highly acidic α-hydrogen in the α-sulfanylated p-substituted benzyl phenyl sulfones suggested the possibility of utilizing this procedure to synthesize deuterated benzaldehydes[20]. In fact, the treatment of these sulfones with sodium hydride in THF, followed by addition of deuterium oxide, afforded quantitatively the corresponding pure α-deuterated sulfones. The pyrolysis of the latter, under the same conditions as employed for the corresponding undeuterated sulfones, yielded 1-deuteriobenzaldehydes of isotopic purity greater than 98%, as indicated by ^1H NMR and mass spectra analyses. Thus, this method provided a general route to p-substituted 1-deuteriobenzaldehydes, irrespectively of the electronic character of the substituents (Scheme 23).



SCHEME 23

It is noteworthy that the thermal decomposition procedure failed to occur for the α-methylsulfanyl alkyl sulfones, but was successful with the α-methylsulfanyl α-alkyl benzyl sulfones to yield phenyl alkyl ketones[21] in 80-90% yield (Scheme 24).

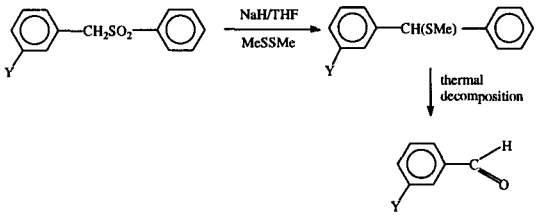
In our further investigations we extended these studies to the α-sulfanylated meta- and ortho-substituted benzylic sulfones, potential intermediates for the syntheses of the m- and o-substituted benzaldehydes[22,23]. In the case of the meta-substituted



Y = H; Me, OMe
R = Me, Et, CH_2SMe, ϕCH_2, $CH_2CH(OEt)_2$

SCHEME 24

derivatives the sulfanylation conditions for their preparation as well as for their decomposition did not differ from those for the corresponding para-substituted derivatives (Scheme 25).

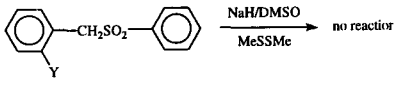


Y = NO_2, OMe, CN

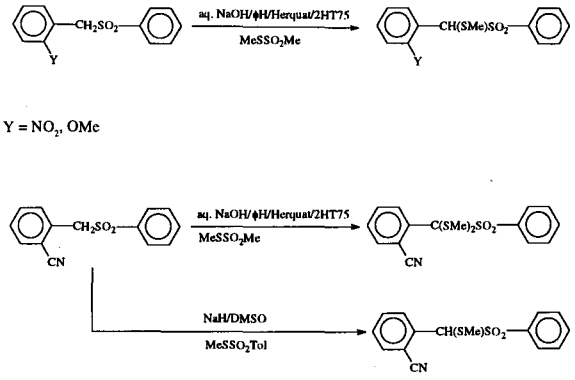
SCHEME 25

However, the corresponding ortho-substituted benzylic sulfones proved to be resistant to the same sulfanylating conditions, as no reaction occured when NaH and dimethyl disulfide were employed.

However, good results were obtained when instead of this homogeneous method the "phase transfer condition" was employed. Thus, using aq. NaOH, benzene, S-methyl methanethiosulfonate as sulfanylating agent, and as catalyst Herquat 2HT75, while ortho-nitro and methoxy derivatives led to the monosulfanylated products, the ortho-cyano derivative afforded the bis-sulfanylated product. However, it was possible to obtain the corresponding mono-sulfanylated ortho-cyanosubstituted derivative in homogeneous medium, using S-methyl p-toluenethiolsulfonate, in the presence of an excess of NaH/DMSO (Scheme 26).



Y = NO_2, OMe, CN

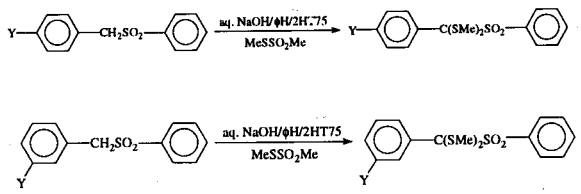


Y = NO_2, OMe

Herquat 2HT75 = dimethyl dialkyl (C_{16}-C_{18}) ammonium chloride

SCHEME 26

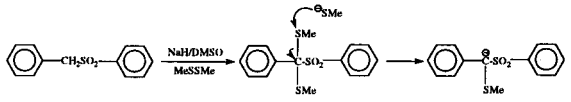
It is noteworthy that when the phase transfer procedure, using S-methyl methane thiosulfonate, was applied to the unsubstituted, para- and meta-substituted benzylic sulfones the disulfanylated derivatives were also obtained (Scheme 27).



SCHEME 27

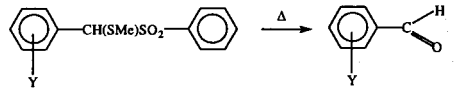
The lack of reactivity of ortho-substituted benzylic sulfones toward dimethyl disulfide was interpreted as due to steric hindrance. Similar explanation was given to the difference in reactivity toward a more powerful reagent S-methyl methanethiosulfonate, which afforded bis-sulfanylated products for para- and meta-derivatives, but mono-sulfanylated products in the case of the corresponding ortho-derivatives. The exceptional behaviour of the ortho-cyano benzylic sulfone, which undergoes bis-sulfanylation, was attributed to the unhindered linear geometry of the cyano group.

The difference in reactivity of para- and meta-substituted sulfones toward dimethyl disulfide and S-methylmethanethiosulfonate leading, respectively, to mono- and bis-sulfanylation, was rationalized by the fact that in both cases initial formation of the bis-sulfanylated derivative occurs but, in the case of dimethyl disulfide, it undergoes desulfanylation through an attack of the ^-SMe leaving group on sulfur, to give a carbanion which survives in DMSO (Scheme 28). In the case of S-methyl methanethiosulfonate the corresponding leaving group would be too hard a nucleophile to promote such desulfanylation.



SCHEME 28

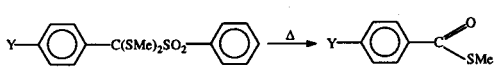
The cleavage of the mono-sulfanylated ortho- and meta- substituted benzylic sulfones to the corresponding carbonyl compounds[22] was performed by the thermal decomposition method at the temperature range of 108-135°C. The corresponding benzaldehydes were obtained in good yields (70-93%) (Scheme 29).



Y-(ortho- and meta-); OMe, NO_2, Me, CN

SCHEME 29

Similarly, the bis-sulfanylated unsubstituted, p-methoxy, and p-nitro-substituted benzylic sulfones were submitted to thermal decomposition[24], to give the corresponding thiobenzoates in 81%, 60% and 67%, respectively (Scheme 30).

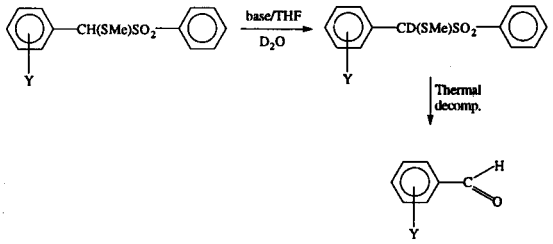


Y = H, OMe, NO_2

SCHEME 30

The monosulfanylated ortho- and meta-substituted benzylic sulfones showed to be also intermediates for the synthesis of the ortho- and meta-deuteriobenzaldehydes[23].

The deuterated sulfones were obtained employing NaH/THF and D_2O with exception of the methoxy derivative, for which a stronger base, BuLi/THF had to be used. The pyrolysis of the deuterated sulfones was performed by heating at 100-135°C, to give the corresponding 1-deuterio benzaldehydes in good yields with ca. 98% isotopic purity (Scheme 31). Therefore, it may be concluded that this method is general for the synthesis of substituted 1-deuterio benzaldehydes, independently of the position and electronic character of substituents.

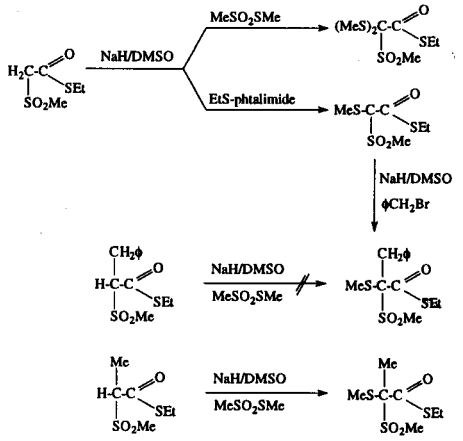


Y = OMe, NO_2, CN

SCHEME 31

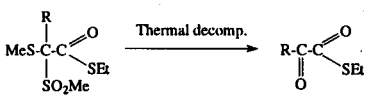
More recently,[25] the pyrolysis method was applied to molecules containing $>C(SR)_2$ system to give the α-keto-thioesters, which as the α-keto-esters are important metabolic intermediates[26,27].

The α-methylthio, α'-methylsulfonyl-thioesters were obtained from the corresponding α-sulfonyl thioesters by sulfanylation reactions (Scheme 32). It was observed that, in the case of the sulfonyl ethylthioacetate, ethylsulfanylphtalimide had to be employed as sulfanylating agent, as S-methyl metanethiosulfonate yielded bis-sulfanylated product. It should be also noted that the sulfanylation of α-benzyl-substituted sulfonyl thioester was unsuccesful, although surprisedly it was possible to introduce the α-benzyl group into the sulfanylated product.



SCHEME 32

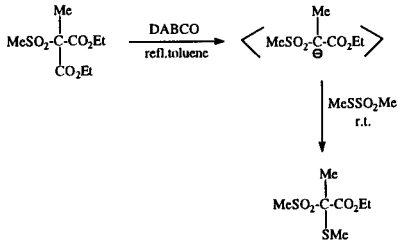
The thermal decomposition of these intermediates yielded the corresponding α-keto-thioesters in good yields. It is noteworthy that in the case of the benzyl substituted derivative, the decomposition occurred at lower temperature (80°C) than in the case of the methyl substituted derivative (Scheme 33).



R = Me, CH_2f

SCHEME 33

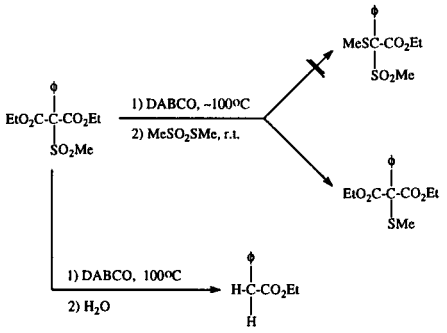
In order to obtain α-keto esters a new method of synthesis of derivatives containing the -C(MeSO$_2$)(SMe)CO$_2$Et group was investigated[28]. It has been reported[29] that the geminal diesters undergo an O-alkyl cleavage followed by decarboxylation when treated with DABCO in refluxing xylene. This reaction was applied to the a-sulfonyl substituted, geminal esters, and the treatment with DABCO was followed by addition of S-methyl methanethiosulfonate. We verified that when the α-methylsulfonyl, α-methyl malonic ester was submitted to thermal decomposition, aprox. 100°C, in the presence of DABCO, and S-methyl methanethiolsulfonate, the sulfanylative decarbethoxylation took place, with formation of the α-methylsulfanyl-methylsulfonyl propanoate in 68% yield (Scheme 34).



SCHEME 34

However, a surprising result was obtained when the α-sulfonyl phenylmalonic ester was submitted to the reaction with the same reagents, under similar reaction conditions. Instead of the expected methylsulfanyl-substituted α-methylsulfonyl ester, the methylsulfanyl-substituted malonic ester was obtained in quantitative yield (Scheme 35). This result indicates that, instead of decarbethoxylative sulfanylation, the dessulfonylative sulfanylation has occurred.

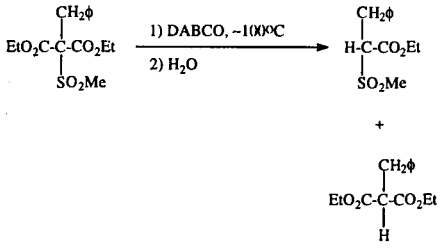
The evidence for the desulfonylation, with formation of carbanion, was obtained when no sulfanylating agent but water was added, and the α-phenylmalonate was isolated.



DABCO = 1,4-diazobiciclo[2,2,2]octane

SCHEME 35

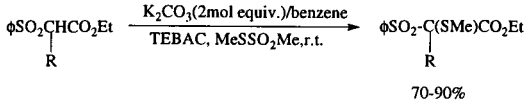
Partial desulfonylation was also observed when α-sulfonyl benzylmalonate was treated with DABCO in refluxing benzene. After addition of water, α-benzylmalonate was obtained in admixture with α-sulfonyl benzylacetate (Scheme 36).



SCHEME 36

Therefore, it may be concluded that this method is not general for the intermediates, containing -C(SMe)(MeSO$_2$)CO$_2$Et system. It seems obvious that there is a gradative change from decarbethoxylation to desulfonylation by going from methyl to benzyl and to phenyl groups in α-position. This is an indication that the site of nucleophilic attack by nitrogen nucleophile depends on the steric acessibility of the eletrophilic center. In the case of desulfonylation, it is difficult to predict whether the center of attack is the carbon or sulfur atom of the MeSO$_2$ group[30].

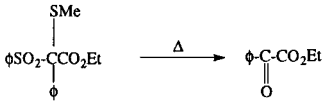
Recent investigation showed[31] that the α-methylsulfanyl sulfonyl esters can be obtained in good yields directly by sulfanylation of the α-sulfonyl esters, by phase transfer procedure, using K$_2$CO$_3$ and TEBA (Scheme 37).



R = H, Me, Et, ϕ, p-Cl-C$_6$H$_4$, p-Me-C$_6$H$_4$, p-MeO-C$_6$H$_4$, p-NO$_2$-C$_6$H$_4$

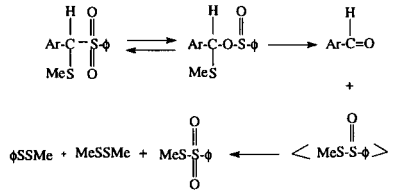
SCHEME 37

It is noteworthy that lower yields were obtained by employing homogeneous procedure[31]. The thermal decomposition of the a-methylsulfanyl sulfonyl esters led to the corresponding α-keto esters in quantitative yield (Scheme 38).



SCHEME 38

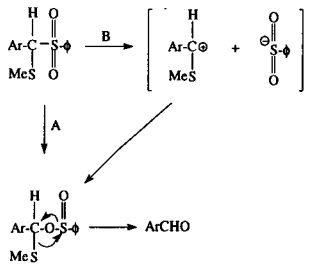
Some comments on the mechanism of the thermal decomposition of compounds containing a >C(SEt)SO$_2$Me system may be added. It was suggested[20] that it occurs through the initial rearrangement of sulfone to sulfinate and that, therefore, the carbonyl oxygen originates from the sulfonyl group. In contrast with the relatively facile thermal rearrangement of sulfinates to sulfones, the reverse process is relatively rarely encountered, and is usually observed only at elevated temperature[32]. In our case the sulfone-sulfinate equilibrium is shifted irreversively to the latter due to its decomposition into benzaldehydes and benzene thiosulfinate, which decomposes again to give thiosulfonate and a mixture of disulfides (Scheme 39).



SCHEME 39

Two possible mechanisms for the first step of this process, i.e. the sulfone-sulfinate rearrangement, have been proposed, either ionic (B) or internally concerted (A) (Scheme 40).

It should be mentioned that in a review[33] were reported some unpublished results on the thermal decomposition of the disulfanylated sulfones, leading to thioesters, which was proved to proceed via an ion-pair mechanism, as well as a similar thermal decomposition of α-mono sulfanylated sulfones leading to the corresponding carbonyl compounds. However, in this latter case, no conclusions were drawn on the ionic or concerted character of the initial sulfone-sulfinate rearrangement.



SCHEME 40

In our case, some experiments seemed to indicate rather a concerted mechanism. Thus, the experiments performed by refluxing in several solvents indicate that the decomposition is very sensitive to the increase of temperature, but not to the increase in solvent polarity.

FINAL REMARKS

It was shown that the gem-dithio-derivatives, containing $-C(R)(SR)_2$, -C(R)(SOR)SR or $-C(R)(SO_2R)SR$ groups, can be considered as synthetic C=O equivalents.

Two types of methods of obtention of such intermediates are reported: 1) Alkylation of the corresponding unsubstituted dithio-derivatives; 2) Sulfanylation of the corresponding monosulfanyl-derivatives. The reactivity of both type of reaction, C-C and C-S formation, increases in the order SR < SOR < SO_2R and may be attributed to the increase of the acidity of the α-hydrogen, due to the increase of the electron withdrawing effect of the sulfur containing group.

As for the decomposition of such intermediates, to yield the carbonyl derivatives, the leaving group effectiveness should be considered. Thus, while in the case of the sulfanyl and sulfinyl group the addition of a Lewis acid or protonation is necessary, in the case of the sulfonyl group the dissociation without any catalysis, under heating, takes place.

Due to these facts the α-alkylsulfanyl sulfones are the appropriate derivatives. It seems reasonable to conclude that the thermal decomposition of α-sulfanyl sulfones is the only decomposition method for obtention of the α-keto esters α-keto thioesters, sensitive to acid.

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