

SHORT
COMMUNICATIONSTransformation of Dimethyl Sulfoxide
into Bis(methylsulfanyl)methane

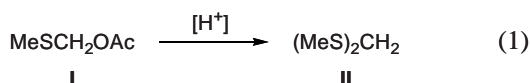
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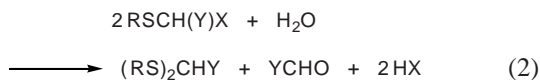
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We recently [1] revealed that methylsulfanyl methyl acetate (**I**), which is readily available from DMSO according to Pummerer [2], is rapidly and quantitatively converted into bis(methylsulfanyl)methane (**II**) in the presence of strong acids.



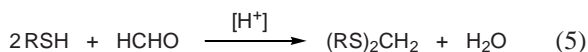
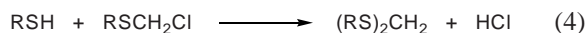
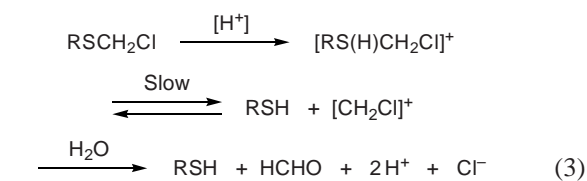
Reaction (1) attracts interest as an example of new and probably general way of synthesis of thioacetals from sulfoxides (cf. [3]), whose mechanism is not clear. The goal of the present work was to elucidate the mechanism of transformation (1) on the basis of published data and demonstrate usefulness and perspectives of the new method of synthesis of thioacetals from sulfoxides.

As shown in [4], α -haloalkyl sulfides of the general formula RSCH(Y)X (where $\text{R} = \text{Alk, Ph, Bzl}$; $\text{X} = \text{Cl, Br, I}$, $\text{Y} = \text{H, Ph}$), which are structurally related to methylsulfanyl methyl acetate, undergo hydrolysis in aqueous dioxane according to Eq. (2); the reaction follows first-order kinetics.

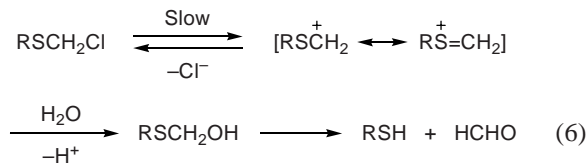


Taking into account that reaction (1) was carried out in aqueous media [1], we can presume that it follows a mechanism analogous to the mechanism proposed in [4], i.e., via hydrolysis to give the corresponding thiol and aldehyde (as a result of cleavage of the C–S bond) in the rate-determining stage. Thiol then reacts with the initial compound [reaction (4)] [4, 5],

as well as with formaldehyde [reaction (5)] [5, 6]; as a result, the corresponding dithioacetal is formed, and the overall stoichiometry conforms to reaction (2).



Böhme et al. [4] assumed that the process involves autocatalysis due to liberation of hydrogen chloride. However, the proposed mechanism was questioned by Bordwell et al. [7] who studied the hydrolysis in 50% aqueous dioxane. These authors advanced $\text{S}_{\text{N}}1$ mechanism with intermediate formation of a carbenium-sulfonium ion in the rate-determining stage and subsequent fast attack by water molecule, leading to dissociation of the hemithioacetal into thiol and aldehyde [8] [reaction (6)]. This mechanism is likely to involve assistance by acid.



As noted in [9], α -acetoxy methyl sulfides RSCH(Y)X (where $\text{R} = \text{Alk, Ar}$; $\text{Y} = \text{H}$; $\text{X} = \text{OAc}$) are readily decomposed by the action of water to give the

corresponding thiol, formaldehyde, and acetic acid. However, we found that hydrolysis of methylsulfanyl-methyl acetate (**I**) with water (1:1) in the absence of sulfuric acid occurs only under severe conditions: the conversion is only 7% in 3 min on heating at the boiling point under vigorous stirring.

Thus, uncertainty and inconsistency of published data do not allow us to draw a definite conclusion on the mechanism of reaction (1). Following the known data, it is unlikely that acid-catalyzed reaction (1) in the final stage can be represented as reaction (5) preceded by transformation sequence (6), for hemithioacetal is an intermediate product on the path to thioacetal which is usually obtained from thiol and aldehyde. Thus the mechanism of transformation (1) requires further study.

The proposed procedure is advantageous since it requires no reduced temperature, highly reactive, volatile, and toxic halogen-containing sulfides, formaldehyde, thiols, and gaseous hydrogen chloride. Initial sulfoxides are readily accessible from sulfides that can be easily prepared in a laboratory or are commercial products [10]. The procedure for the synthesis of thioacetals from sulfoxides is simple and efficient, as illustrated below by the synthesis of bis(methylsulfanyl)methane from DMSO as an example. As concerns the selectivity aspect, it should be examined separately for each particular sulfoxide involved in the reaction.

Bis(methylsulfanyl)methane (II). A mixture of 25 ml (25 g, 0.32 mol) of anhydrous dimethyl sulfoxide and 43.9 g (0.43 mol) of acetic anhydride was heated to 130°C; the mixture vigorously boiled up and was kept for 1 h at that temperature. It was then cooled to room temperature, and 50 ml of 51% sulfuric acid was added on stirring and cooling. The resulting solution was kept for 5 min and diluted with 50 ml of water, 20 g of sodium sulfate was added, and the mixture was stirred until the salt dissolved completely. The mixture was allowed to settle down, and the organic phase was separated, washed with 20 ml of water, and dried over anhydrous MgSO₄. Yield 17.2 g (98%), bp 147°C, $n_D^{20} = 1.5340$, $d_4^{20} = 1.059$ (cf. [11]). ¹H NMR spectrum, δ , ppm: 2.11 s (6H, CH₃), 3.66 s (2H, CH₂) (cf. [12]). Found, %: C 32.96; H 7.49; S 55.54. C₃H₈S₂. Calculated, %: C 33.29; H 7.46; S 59.23.

The ¹H NMR spectrum was recorded on a Gemini-200 spectrometer at 200 MHz using CD₃CN as solvent and TMS as internal reference. Methylsulfanylmethyl acetate (**I**) was synthesized according to the procedure reported in [2]. The conversion of compound **I** in the

hydrolysis with boiling water was determined by GLC (internal standard technique with tridecane as reference). GLC analysis was performed on an LKhM-80 model 6 chromatograph [flame ionization detector; stainless steel column, 3000×3 mm, packed with 5% of QF-1 on Inerton Super (0.16–0.20 mm); carrier gas helium; oven temperature 140°C.

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