

THERMOLYSIS OF ETHYLENE EPISULFOXIDE IN METHANOL.
PUMMERER TYPE REARRANGEMENT OF THIOLSULFINATES

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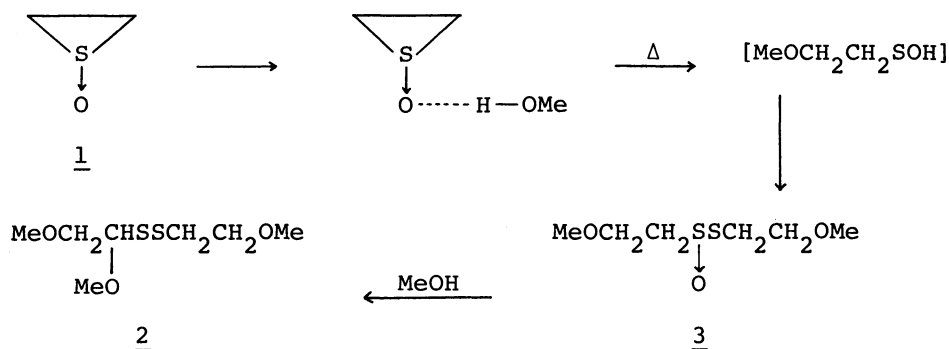
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The thermal reaction of ethylene episulfoxide in methanol at 90°C gave 2-methoxyethyl 2-methoxyethanethiolsulfinate as a primary product which was further transformed into 1,2,2'-trimethoxydiethyl disulfide. This type of Pummerer rearrangement could also be observed when ethyl ethanethiolsulfinate or 2-acetoxyethyl 2-acetoxyethanethiolsulfinate was treated under the same condition.

Thermolysis of an episulfoxide usually affords an olefin and sulfur monoxide.¹⁻⁴⁾ Some special episulfoxides are also known to undergo intramolecular rearrangement under thermal condition.^{5,6)} We have now found a new thermal reaction of an episulfoxide in methanol which affords an α -methoxy disulfide as the final product. The reaction seems to have some implication on the scission of a carbon-sulfur bond in disulfide systems of biochemical interest.

No reaction occurred when ethylene episulfoxide (1) was refluxed in methanol for 5 hr. However, on heating in methanol at 90°C for 15 hr in a sealed tube, 1 was cleanly transformed into 1,2,2'-trimethoxydiethyl disulfide (2)⁷⁾ in 85% yield. In order to elucidate the mechanism of the formation of 2, the following two control experiments were run. Firstly, the methanolic solution of 1 was refluxed for a prolonged time (50 hr). Careful fractionation of the reaction mixture through column chromatography on silica gel gave 2-methoxyethyl 2-methoxyethanethiolsulfinate (3)⁸⁾ (13%), in addition to 2 (9%) and unreacted 1 (64%). Secondly, the thiolsulfinate 3 was held at 90°C for 20 hr in a sealed tube. Under this condition, 3 was completely transformed into the α -methoxy disulfide 2 in almost quantitative yield. The mechanism shown in the following scheme may accommodate all of these observations. In the solution, the sulfoxide oxygen of 1 should be strongly solvated by methanol through hydrogen bonding. The heterolytic scission of carbon-sulfur bond at elevated temperature might be



assisted by this hydrogen bonding as well as the inherent strain of the three-membered ring and will result in the formation of unstable 2-methoxyethanesulfenic acid. Dehydrative dimerization of the sulfenic acid produces the thioisulfinate 3.⁹⁾ In general, thioisulfates are relatively unstable compounds and readily disproportionate to a mixture of disulfide and thioisulfonate.¹⁰⁾ However, under the aforementioned condition, 3 was quantitatively transformed into the disulfide 2 by the Pummerer type rearrangement.^{11,12)} In order to ascertain the generality of this reaction, we have now investigated the reaction of thioisulfates 4 and 5¹³⁾ under the similar conditions. As summarized in Table I, α -methoxy disulfides 6 and 7¹⁴⁾ were obtained in excellent yields. The results clearly indicated that the Pummerer type rearrangement of thioisulfates does really occur efficiently in methanol at 90°C.

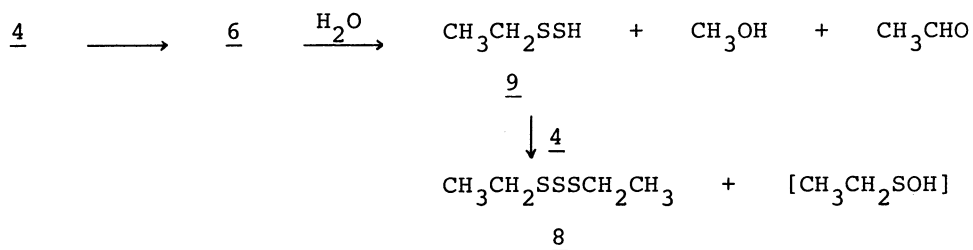
Table I. Thermal Rearrangement of Thioisulfates $\text{XCH}_2\text{CH}_2\text{SSCH}_2\text{CH}_2\text{X}$ to α -methoxy disulfides $\text{XCH}_2\text{CH}(\text{MeO})\text{SSCH}_2\text{CH}_2\text{X}$

Thioisulfate	Reaction ^a Time (hr)	Disulfide	Yield ^b (%)	B.p. °C (Torr)
<u>3</u> X=MeO	20	<u>2</u>	94	71 (0.2)
<u>4</u> X=H	9	<u>6</u>	97	78 (12)
<u>5</u> X=AcO	13	<u>7</u>	90	132 (0.2)

^a The temperature of the reaction mixture was held at 90°C.

^b Yields were determined by glc analyses using a 1m x 8mm stainless steel column packed with 10% Carbowax 20M on Chromosorb W.

When the thiolsulfinate 4 was dissolved in methanol containing 10%(v/v) of water and heated under the same conditions described above, diethyl trisulfide (8) was formed in 60% yield along with the rearranged disulfide 6 (27%). A possible explanation for the formation of the trisulfide 8 is as follows : hydrolysis of 6 may give acetaldehyde, methanol, and ethyl hydrogendisulfide (9) and the latter will attack on sulfur of an unreacted thiolsulfinate 4 to produce 8. The reaction may be noteworthy with regard to the scission of carbon-sulfur bond in thiolsulfinites. Kice and his associates¹⁵⁾ investigated thoroughly the cleavage reaction of the sulfur-sulfur bond in thiolsulfinites as a model for the scission of a sulfur-sulfur bond in biochemical systems. However, under oxidative conditions, the disulfide in cystine undergoes not only the scission of its sulfur-sulfur bond but also that of carbon-sulfur bond and in some special cases affords a trisulfide as the final product.¹⁶⁾ Our result seems to provide an interesting and valuable suggestion for this reaction.



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