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THE ACID CATALYZED RING OPENING REACTION OF EPISULFOXIDES

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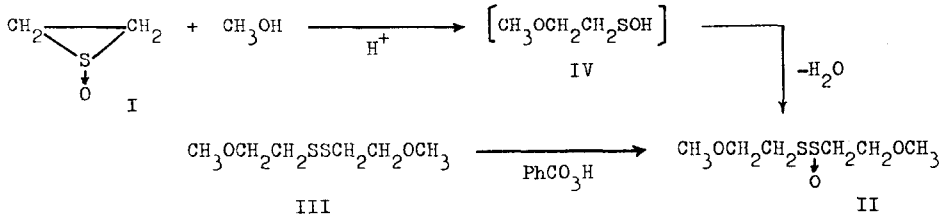
Continuing our study of the chemistry of episulfoxides (1,2), we reinvestigated the titled reaction of ethylene episulfoxide (I), which had been reported by Hartzell and Paige (3). Contrary to their assumption for the reaction product, it was proved to be β-methoxyethyl β-methoxyethanethiolsulfinate (II).

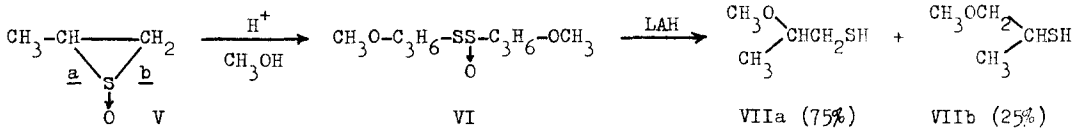
A solution of I in methanol was treated with one drop of concentrated sulfuric acid at 0-5°. The tlc of the reaction mixture indicated the complete disappearance of I and the formation of a new substance after 3 hr reaction. The structure of the product isolated in 96% yield was identified as II by the following spectral data and elemental analysis: ir(cm^{-1}); 1115 and 1080. nmr(τ); 6.3(4H, m), 6.66(6H, s), and 6.8(4H, m). Calcd. for $C_6H_{14}O_3S_2$; S 32.34, Found; S 32.29%. The final confirmation of the structure was obtained by synthesizing II independently. Thus, the oxidation of bis(β-methoxyethyl)disulfide (III) with equimolar perbenzoic acid afforded II in 80% yield, which showed exactly identical spectra with those of II derived from I.



The formation of II can easily be rationalized by assuming the intermediacy of β-methoxyethanesulfenic acid (IV), which will be formed by the nucleophilic attack of methanol to protonated episulfoxide. The dehydrative coupling of a sulfenic acid to afford a thiolsulfinate has ample precedents (4).

A kinetic study of the perchloric acid catalyzed hydrolysis of ethylene episulfoxide (I)

was done by Manser et al. (5), who proposed that the ring opening reaction proceeded by a bimolecular A-2 mechanism. The products obtained by the acid catalyzed methanolyses of substituted episulfoxides, however, appear to favor an A-1 mechanism. A similar treatment of propylene episulfoxide (V) in methanol in the presence of sulfuric acid afforded a mixture of isomeric thiolsulfinates VI in a quantitative yield. The ratio of the respective product resulting from bond a or bond b cleavage was determined at the stage of mercaptans VII which was obtained in 77% yield by reducing VI with lithium aluminum hydride.



V VI VIIa (75%) VIIb (25%)

Vpc analysis (10% dioctyl phthalate, 1 m, 60°) indicated that VII consisted of two components in the ratio of 75:25. Each of the mercaptans was isolated by preparative vpc and their structures were established unequivocally by the following spectra and analyses: nmr(τ); thiol proton in VIIa at 8.67(t) and VIIb at 8.73(d). mass(m/e); VIIa at 106(M^+) and 59 ($[CH_3O{=}CHCH_3]^+$, base peak), and VIIb at 106(M^+) and 45($[CH_3O{=}CH_2]^+$, base peak). The formation of VIIa as a major component clearly suggests that the rate determining step of the reaction is the formation of carbonium ion from protonated V.

The acid catalyzed methanolyses of styrene and isobutene episulfoxide yielded the thiolsulfinates VIII and IX of the following structures in 81 and 79% yields, respectively. These results also favor the A-1 mechanism for the ring opening reaction.

VIII IX

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