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THE OXIDATIVE RING OPENING REACTION OF ETHYLENE EPISULFOXIDE BY COPPER(II) HALIDES

Kiyosi Kondo, Akira Negishi and Gen-ichi Tsuchihashi
Sagami Chemical Research Center
3100 Onuma, Sagamihara, 229 JAPAN

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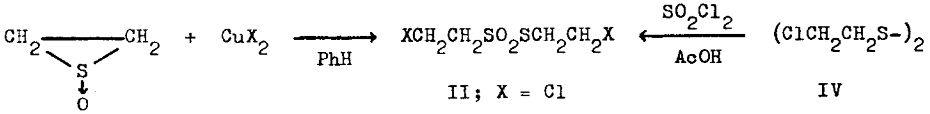
The increased availability of ethylene episulfoxide (I) (1) has led us to investigate the reaction of this unique heterocyclic compound with other substrates (2). One of the representative behaviors of sulfoxides is the formation of complexes with various metal salts (3). Unexpectedly, however, treatment of I with copper(II) halides afforded ring opened products, whereas dimethyl sulfoxide gave stable colored complexes (4). In the present letter we wish to report some details of this new type of reaction which appears to proceed according to a cationic mechanism.

When ethylene episulfoxide (I) was added to a suspension of copper(II) chloride (eq. mole) in benzene at room temperature, the metal salt was reduced quantitatively to copper(I) chloride. Concentration of the organic layer afforded β-chloroethyl β-chloroethanethiolsulfonate (II), b.p. 125°/1 mm., in 65.5% yield, which crystallized on standing at 5°, m.p. 33°. The same treatment of I with copper(II) bromide gave the dibromo analog (III), m.p. 43°, in 64.2% yield. The structures of II and III were supported by spectroscopic data and elemental analyses, and confirmed finally by synthesizing II independently. Thus, the oxidation of bis(β-chloroethyl)disulfide (IV) with sulfuryl chloride in acetic acid (5) afforded II in 70% yield, which showed exactly identical spectra with those of II derived from I.



I

II; X = Cl

III; X = Br

IV

In a second set of experiments, the reaction of I with copper(II) salts was carried out in absolute alcohols below 0^{o}. Two moles of the salt was necessitated for the complete disappearance of the sulfoxide. As the reaction proceeded, the color of the solution changed from green to colorless, and the formations of copper(I) salt and fumes of hydrogen halide were observed. In order to remove the gaseous acid which is known to catalyze the different type of ring opening of I (6), the reaction mixture was flashed with dry nitrogen throughout the course of the reaction. The evaporation of the solvent gave alkyl β-haloethanesulfinate (V) as a major product. The results are summarized in Table I. The structure of V was identified by spectra and analyses. The presence of an asymmetric sulfinyl group was clearly demonstrated in the nmr spectrum of isopropyl ester Vc, which showed the absorption of diastereotopic methyl protons (7) in the ester as two doublets at τ 8.6 and 8.7.

Either β-haloethanesulfinyl radical, $XCH_2CH_2\dot{S}O$ (A) or the cation, $XCH_2CH_2\overset{+}{S}O$ (B) is presumed to be a potential intermediate of the reaction. Although sulfinyl radicals are known to give thiolsulfonates by dimerization (8), speculation about the mechanism involving the cation B as the most probable intermediate was obtained from the following observations.

When the reaction of I with copper(II) chloride was carried out in methylene chloride containing a trace amount of methanol, methyl β-chloroethanesulfinate (Va) was obtained

Table I

β-Haloethanesulfinates from Ethylene Episulfoxide

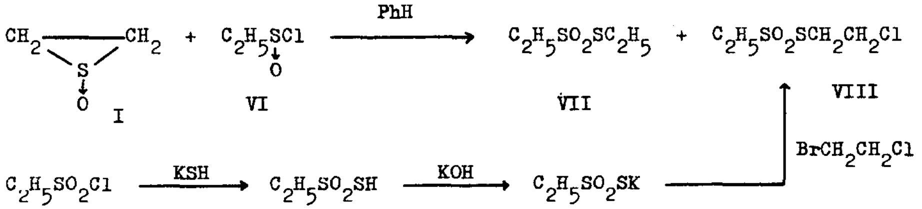
$$\underset{\text{I}}{C_2H_4SO} + 2CuX_2 + ROH \longrightarrow \underset{\text{V}}{XCH_2CH_2S(O)OR} + 2CuX + HX$$

V	R	X	Yield %	B.p. °C/mm.	IR cm^{-1}	Anal. (%) Found S	Calcd. S
a	CH_3	Cl	75	63/3.5	1135, 995	22.12	22.48
b	C_2H_5	Cl	95	61.5/1.5	1137, 1015	20.78	20.47
c	$\underline{i}$-C_3H_7	Cl	78	44/0.1	1140	19.00	18.79
d	CH_3	Br	86	50-60/0.1	1128, 990	17.14	17.14
e	C_2H_5	Br	60	50-60/0.01	1130, 1015	15.93	15.95

as a sole product. The same reaction in benzene in the presence of various olefins including ethyl vinyl ether, acrylonitrile, or cyclohexene yielded II in good yield and no addition products of radical A to these olefins could be isolated.

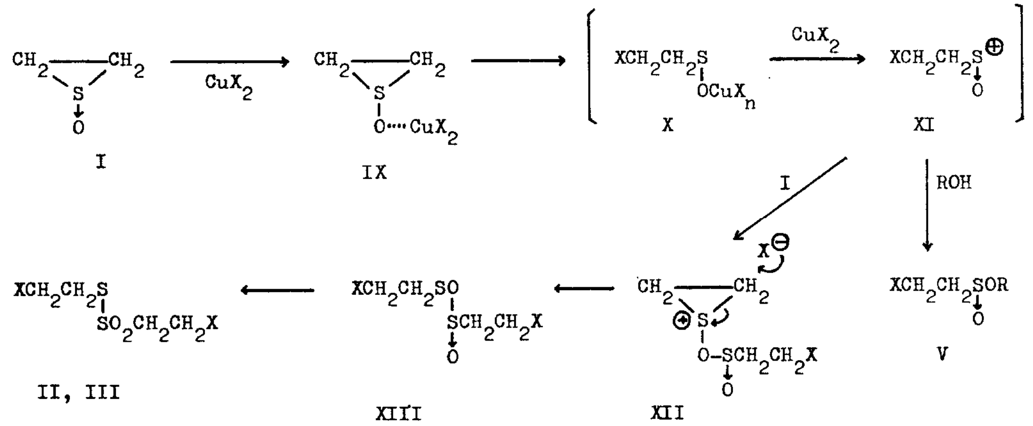
The formation of the sulfinate V in alcohols can easily be understood by assuming the intermediacy of the sulfinyl cation B. However, the intriguing transformation of the cation into thiolsulfonates II and III appears to be without precedent.

To demonstrate that sulfinyl cations do attack the sulfoxide group, the reaction of I with ethanesulfinyl chloride (VI) in benzene was undertaken. The resulting product was a mixture of thiolsulfonates, VII (20%) and VIII (80%). Although it failed to separate the mixture by fractional distillation or column chromatography, the ratio of the two could be determined from nmr intensities. The structures of these thiolsulfonates were confirmed by comparing their nmr peaks with those of authentic samples. A pure sample of VII was obtained by hydrolyzing VI, whereas VIII was synthesized from ethanesulfonyl chloride according to the following sequence.



Thus, β-haloethanesulfinyl cation (B) is considered to be a general reacting species in both protic and non-protic solvents. The remaining question is how this cationic species can be generated by the interaction of the sulfoxide I with copper(II) halides.

Since sodium chloride or lithium chloride did not promote the reaction, we believe that the ring opening is initiated by the coordination of the sulfoxide oxygen to copper(II) metal (IX). The nucleophilic attack of halide anion onto the ring would be facilitated by this coordination, resulting in the formation of copper sulfenate (X). As all the attempts to quench X at this stage have failed, the oxidation of X by copper(II) salt to sulfinyl cation (XI) or its equivalent, e.g., the sulfinyl chloride, should be a fast process. In alcoholic solvents, XI will be transformed into the sulfinate V, while in non-protic solvent, XI will react with the episulfoxide to give episulfonium (XII). The nucleophilic attack of the halide anion to XII should result in the formation of the thiolsulfonates II and III via mixed anhydride XIII. The rearrangement of sulfenic-sulfinic anhydride to thiolsulfonate has a precedent (9).



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