

The Reaction of Cuprous Ethanethiolate with 1,2-Dibromoethylene

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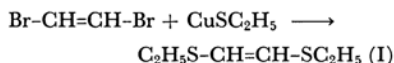
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In 1959, Adams and Ferretti¹⁾ reported that *S*-ethyl hydrogen thiocarbonate was formed by the oxidation of ethyl ethynyl sulfide, which had been obtained from the reaction between 1,2-dibromoethylene and cuprous ethanethiolate, with hydrogen peroxide. It is generally accepted that the thiocarbonic acid and their primary esters are exceedingly unstable in the free state, but their derivatives, such as salts, neutral esters and amides, are sufficiently stable.

Since the observation of Adams and Ferretti about the stability of *S*-ethyl hydrogen thiocarbonate seems unusual, we have repeated their experiments; we have found that the reaction between 1,2-dibromoethylene and cuprous ethanethiolate does not lead to ethyl ethynyl sulfide, but to 1,2-bis-ethylthioethylene, which is subsequently converted to the corresponding sulfone by oxidation.

The reaction of cuprous ethanethiolate with commercial 1,2-dibromoethylene*¹ was carried out according to the reported procedure.¹⁾ The product I, b. p. 104–108°C at 18 mmHg, was isolated in a 49% yield, while a large amount of tarry material remained:



The infrared spectrum of I was similar to that of Adams and Ferretti's product (b. p. 61°C at 1 mmHg), which they assumed to be ethyl ethynyl sulfide. It showed a strong band at 1260 cm⁻¹, but not those absorptions at 3300 cm⁻¹ and 2100–2140 cm⁻¹ which are characteristic of mono-substituted acetylenes. The results of elementary analysis (Found: C, 48.37; H, 8.06; S, 43.35), Calcd. for C₆H₁₂S₂: C, 48.63; H, 8.16; S, 43.25%, gas chromatography*² and NMR spectrum (3.90 τ(s), 3.93 τ(s), 7.29 τ(q), 7.33 τ(q), 8.70 τ(t), 8.72 τ(t)) indicated that I was a mixture of about equal amounts of two stereoisomeric 1,2-bis-ethylthioethylenes. When I was oxidized with hydrogen peroxide in acetic acid as reported before, two isomeric products were isolated; they were then purified by recrystallization from ethanol. The first product II, m. p. 145–146°C, is less soluble than the second product III, m. p. 90–91°C, which is easily soluble in water. The yields were 35% and 41% respectively. The analysis leads to identical empirical formulas (C₂H₅O₂S) for both products; the would-be *S*-ethyl hydrogen thiocarbonate, m. p. 145–146°C, prepared by

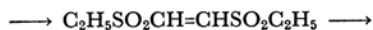
1) R. Adams and A. Ferretti, *J. Am. Chem. Soc.*, **81**, 4927 (1959).

*¹ Infrared spectrum and NMR spectrum showed that the material is a mixture of about equal amount of *cis* and *trans* form.

*² Gas chromatography on Silicon DC 550 column (1 m.) with hydrogen as carrier gas at 100°C showed two peaks with about equal peak-height.

Adams and Ferretti¹⁾ also gives the same formula. These facts demonstrate that II is apparently identical with the Adams and Ferretti's product. Both of the isomers thus obtained are neutral substances, and they show two strong bands, at 1310 cm^{-1} and 1120 cm^{-1} , in the infrared spectrum, which can be assigned to the stretching vibration of a sulfone group.

When both isomers are hydrogenated over palladium-carbon, one mole of hydrogen was absorbed easily, yielding a theoretical amount of 1,2-bis-ethylsulfonylethane, m. p. $137\text{--}139^\circ\text{C}$, which does not depress the melting point of the authentic sample.²⁾



(II): *trans* $\text{C}_2\text{H}_5\text{SO}_2\text{CH}_2\text{CH}_2\text{SO}_2\text{C}_2\text{H}_5$

(III): *cis*

2) Beckman, *J. Prakt. Chem.*, **17**, 469 (1878).

From these results, we may conclude that II and III are geometrical isomers³⁾ of 1,2-bis-ethylsulfonylethylene.

Boonstra and Rinzema⁴⁾ reported that ethyl ethynyl sulfide⁵⁾ shows characteristic bands at 3330 cm^{-1} and 2040 cm^{-1} in the infrared spectrum. From these findings, it is evident that the Adams and Ferretti's products are 1,2-bis-ethylthioethylene and *trans*-1,2-bis-ethylsulfonylethylene, but not ethyl ethynyl sulfide and *S*-ethyl hydrogen thiocarbonate. It is also shown that the reaction of 1,2-dibromoethylene with cuprous ethanethiolate proceeds in the same way as that with cuprous thiophenolate.¹⁾

3) M. F. Shostakovskii, E. N. Prilezhaeva, L. V. Tsymbal and L. G. Stolyarova, *Zh. Obshch. Khim.*, **30**, 3143 (1960).

4) H. J. Bonstra and L. C. Rinzema, *Rec. Trav. Chim.*, **79**, 962 (1960).

5) J. F. Arens and T. Doornbos, *ibid.*, **75**, 481 (1956) and other papers of J. F. Arens et al.