

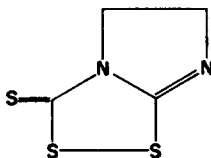
STRUCTURE OF ETHYLENETHIURAM MONOSULFIDE

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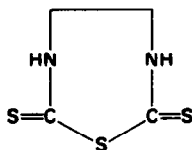
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In a recent communication(1), a new structure for ethylenethiuram monosulfide (ETM, I) was proposed. Further evidence for this structure is presented.

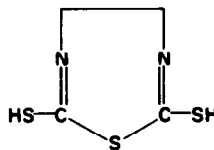


(I)

The older, commonly accepted structure (II) had been arrived at by Thorn and Ludwig(2,3) principally on the basis of infrared analysis although they preferred the enethiol tautomer (III)



(II)



(III)

since the IR showed evidence for C=N ( $\nu = 1615 \text{ cm}^{-1}$ ), absence of an NH vibration at  $3200 \text{ cm}^{-1}$ , and the absence of a "thioureide" ( $-\text{NHC(S)S}-$ ) absorption in the region of  $1510-1470 \text{ cm}^{-1}$ . One disturbing feature of the IR data was the absence of an S-H vibration in the  $2600-2550 \text{ cm}^{-1}$  region. These IR assignments are reasonable for structure I.

During our work with dithiocarbamates, we had noticed anomalous behavior of ethylenethiuram monosulfide. The compound failed to react with Grote's reagent under acidic conditions(4) to give the blue color characteristic of the thiourylene group (NHC(S)NH) or its enethiol tautomer, and it was easily reducible at the dropping mercury electrode(5). Both these observations were unexpected for structures II or III but were rendered plausible on the basis of structure I. We wish to report some of our work which substantiates structure I.

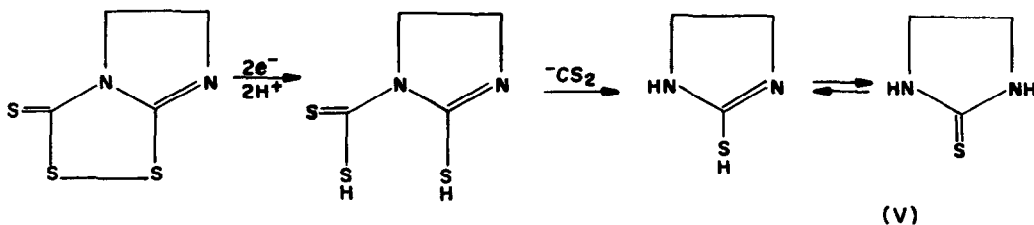
The  $^{13}\text{C}$ -NMR spectrum (run at 25.2 MHz in  $\text{CDCl}_3$  on a Varian XL-100 spectrometer) showed four peaks relative to TMS which have been assigned to C=S (184 ppm), C=N (163 ppm), and  $\text{CH}_2$  groups bonded to nitrogen (48 and 64 ppm). Assignments were made by noting the relative signal enhancement of protonated carbons due to the Nuclear Overhauser effect and the expected longer relaxation times ( $T_1$ ) for the C=S and C=N groups in addition to chemical shifts. The spectrum was consistent with the presence of four nonequivalent carbons as in structure I or possibly IV but not with structures II or III.



(IV)

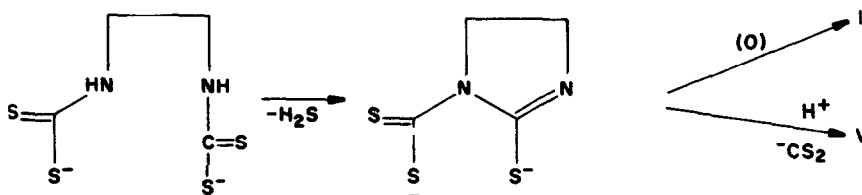
The compound was electrochemically reduced at a controlled potential mercury cathode (-0.45 v. vs. saturated calomel electrode) with a Numec Coulometric Titrator and a three compartment electrolysis cell(6). The sample (15 mg) was dissolved in 10 ml  $\text{CS}_2$  and added to the cathode compartment containing 50 ml 0.1 F  $\text{H}_3\text{PO}_4$ /i-PrOH and 20 ml 0.1 F  $\text{NH}_4\text{Cl}$  (polarographic  $E_{1/2}$  of I = -0.45 v. vs. saturated calomel electrode). The supporting electrolytes solution served

as a bridge and hydrazine sulfate was added to the anode compartment as depolarizer. Structure I might be expected to reduce according to the reaction

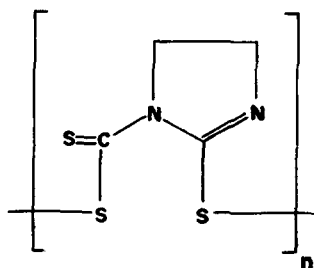


to give ethylenethiourea (V). After electrolysis, the catholyte gave a positive test with Grote's reagent for  $\text{-NHC(S)NH-}$  and analysis by mass spectrometry indicated formation of V. Such electrochemical behavior would not be expected for II or IV.

The proposed structure I suggests explanations for the occurrence of V in ethylenebis(dithiocarbamates), a current problem in the area of fungicides, i.e.,



and a possible structure for polymers obtained upon air oxidation of ethylenebis(dithiocarbamates) (3),



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References:

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