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4-AMINO-3-CARBETHOXYMETHYLENE-1,2-DITHIOLE HYDROCHLORIDE, A NEW NO-BOND RESONANCE COMPOUND

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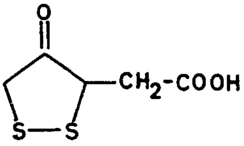
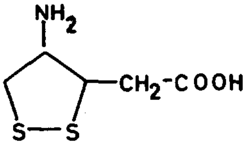
In a previous communication the synthesis of 1,2-dithiolan-4-one-3-acetic acid (I) has been reported (1). Several attempts to prepare the corresponding 4-amino-1,2-dithiolan-3-acetic acid (II) have not given the desired product (2).

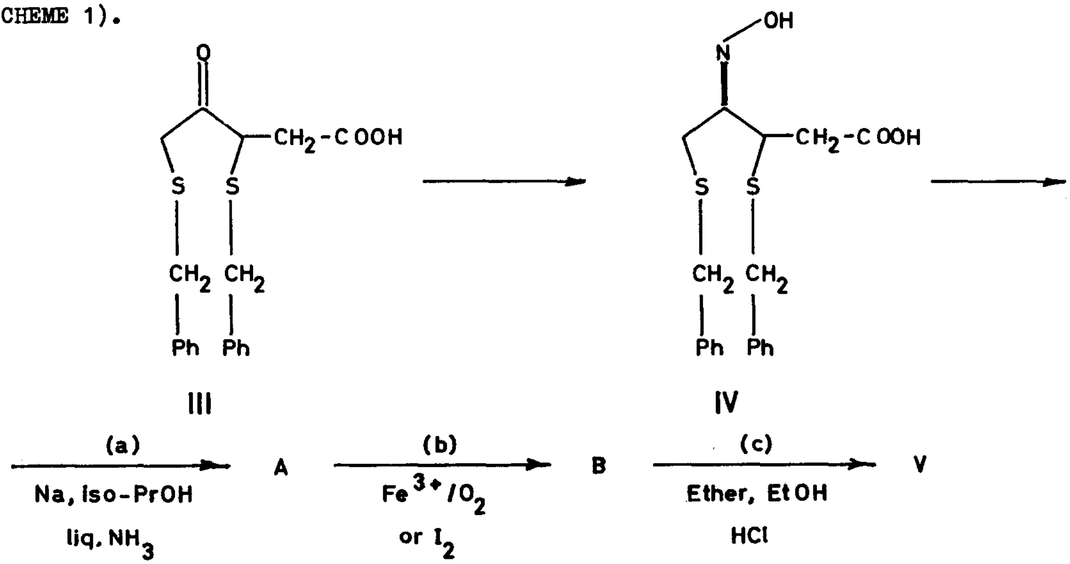


I



II

We wish to describe here the product isolated from one of these attempts (SCHEME 1).



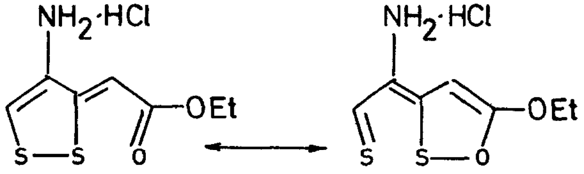
SCHEME 1

The oxime (IV) of 3,5-dibenzylthio-levulinic acid (III) constituted an easily available starting material (1,2). It has been shown that reduction of oximes with sodium and methanol in liquid ammonia leads to primary amines in good yields (3). We therefore hoped that the reaction step (a) would accomplish both debenzylation and reduction of the oximo group to a primary amine. The oxidation shown in step (b) would then ring-close the expected aminodimercapto acid to the cyclic disulphide (II), which by reaction step (c) would be isolated as the hydrochloride of its ester (cf. 4).

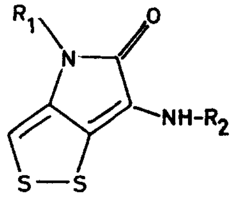
The final reaction product (V), a hydrochloride (crude yield 48%), was purified by several recrystallizations from ethanol. Brass coloured crystals with m.p. 158-162^0 were obtained. These show, however, properties which cannot be ascribed to the 4-amino-1,2-dithiolane ring system.

The elemental analysis and equivalent weights are in agreement with the formula $C_7H_{10}ClNO_2S_2$, which contains four hydrogens less than the formula for the expected product. The ultraviolet absorption spectrum of (V) shows a strong peak at 400 mμ (ε 12130). The compound has infrared absorption bands at 3040 cm^{-1} and 3000 cm^{-1}, suggesting aromatic hydrogens, but lacks the normal carbonyl absorption for an ester. The free amine of V shows infrared absorption bands at 3440 cm^{-1}, 3360 cm^{-1}, 1635 cm^{-1}, 1610 cm^{-1}, 1560 cm^{-1}, and 1510 cm^{-1} in chloroform solution. The nuclear magnetic resonance spectrum of the free amine was studied in deuterochloroform and shows a triplet at τ 8,67 (relative area 3, methyl protons of ethyl ester), a broad peak at τ 6,37 (relative area 2, amino protons), a quartet at τ 5,67 (relative area 2, methylene protons of ethyl ester), a singlet at τ 4,05 (relative area 1), and a singlet at τ 3,33 (relative area 1).

All these data are consistent with the structure shown for compound (V), a "no-bond resonance" stabilized oxygen analogue of the 6a-thiathiophthen ring structure (5).



V



VI

The intermediates (A) and (B) are being investigated, as well as the possibility of utilizing this reaction path to synthesize Thiolutin type (VI) antibiotics.

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