A Dimer of 3-Amino-2-cyano-3-hydroxydithioacrylic Acid

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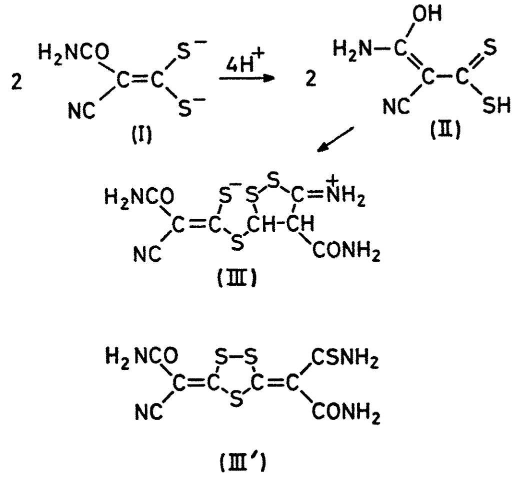
Summary The spontaneous dimerization, in solution, of 3-amino-2-cyano-3-hydroxydithioacrylic acid (II) is demonstrated and a 1,2-dithiolan structure (III) is assigned to the dimer.

WHEN the sodium salt of 2-carbamoyl-2-cyanoethylene-1,1-dithiolate (I) is treated with cold aqueous hydrochloric acid, 3-amino-2-cyano-3-hydroxydithioacrylic acid (II)† is formed (see Scheme 1). This strongly acidic compound is unstable in solution and is, according to pH measurements, transformed into a material with only slight acidic character within *ca.* 20 min. at room temp. The latter material (90%) separated from aqueous methanol and proved to have the same elemental composition as (II).



SCHEME 1

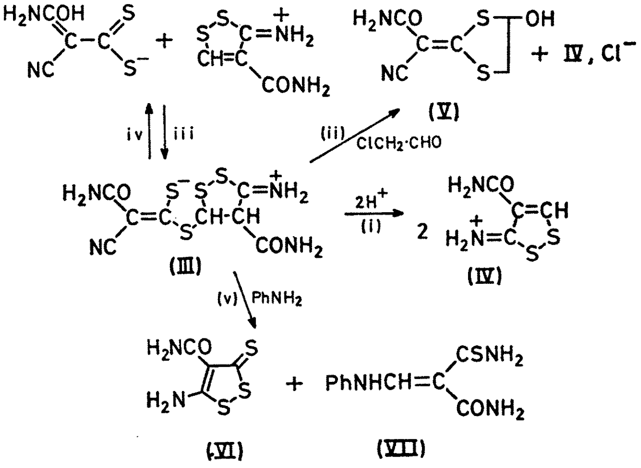
With the support of the following evidence we have assigned the structure (III), corresponding to a dimer of compound (II), to the material isolated.

Cryoscopic measurements in Me$_2$SO showed an apparent molecular weight for (III) in the region of 250—290 [calculated for a dimer of (II): 320]. The observed values were dependent upon the length of time elapsing between the dissolution and the measurement; it was confirmed by conductometric studies in Me$_2$SO that a partial dissociation of (III) into ionic species took place over a period of *ca.* 90 min.

The i.r. spectrum of the dimer (KBr disc) indicated the presence of a conjugated nitrile group (2215 cm.$^{-1}$), two amide groups (1680, 1660, and 1590 cm.$^{-1}$; amide I and II bands) and an X(Y)C=C(S)S grouping (1470 cm.$^{-1}$).[1] The n.m.r. spectrum [(CD$_3$)$_2$SO] showed signals due to 8 protons: four broad singlets [τ 0·05—0·25 (1 H), 0·65—0·85 (1 H), 2·20—2·45 (2 H), and 2·50—2·80 (2 H)], and one AB system [τ 4·02 and 5·90, doublets, *J* 11·5 Hz (1 H each)].

The spectroscopic data are consistent with the dimer having either structure (III) or (III′). The reactions (i)—(v), summarized in Scheme 2, suggest that the structure (III) is the more likely one. However, since a ready interconversion between structures (III) and (III′) might take place during the reactions, the structure (III′) cannot be entirely dismissed.

(i) The formation of the 4-carbamoyl-3*H*-1,2-dithiol-3-yliminium ion (IV) (92%, isolated as a monohydrate of the chloride) with an excess of hydrochloric acid is presumably due to protonation on the thiolate group of (III) followed by dissociation with the formation of (IV) and (II). As shown, the latter species undergoes dimerization to form (III) which re-enters into the reaction. (ii) The reaction of (III) with chloroacetaldehyde consists of *S*-alkylation followed by dissociation into (IV) (68%) and formylmethylated (II), which in turn cyclizes to give the observed dithiolanol (V) (85%). (iii) Compound (III) (91%) was obtained when aqueous solutions of (I) and the hydrogen sulphate of (IV) were added simultaneously to aqueous methanol. [Compound (III) might be formed under these conditions by the action, on (I), of the latter salt in its capacity of a strong acid. However, if this were the case at most a 50% yield could be obtained]. (iv) The reversal of process (iii) is probably responsible for the observed conductivity of a Me$_2$SO solution of (III). This assumption was supported when the n.m.r. spectrum of (III) in (CD$_3$)$_2$SO was recorded 2 hr. after the dissolution. The only change observed, apart from a general broadening of the NH signals, was the appearance of a peak (τ 0·33, intensity *ca.* 15% of each of the doublets) which was shown to coincide with the CH signal of cation (IV). (v) When (III) was treated with aniline, 5-amino-3-thioxo-3*H*-1,2-dithiole-4-carboxamide



SCHEME 2

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† Satisfactory analytical data were obtained for all new compounds and their i.r. and n.m.r. spectra were consistent with the assigned structures.

(VI)[2] (84%) and phenylaminomethylenemonothiomalonamide (VII) (86%) were obtained. The reaction is presumably initiated by a nucleophilic attack by the aniline on C-5 of the 1,2-dithiolan ring. The subsequent rearrangement of the bonds to the sulphur atoms is not clearly understood.

This reaction is of interest because it suggests that the formation of (VI) from (I) with acetic acid in aqueous methanol which was reported by Gewald[3] also takes place *via* (III). Thus the reaction sequence leading to the formation of (VI) from (I) may represent an example of an intermolecular transfer of a sulphur atom without the intervention of elementary sulphur.

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[2] K. Gewald, *J. prakt. Chem.*, 1966, **31**, 214.
[3] K. Gewald, *Chem. Ber.*, 1968, **101**, 383.