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# Hydrolysis of 6,6-Dimethyl-4,8-dioxo-5,7-dioxaspiro[2.5]octane-1,1,2,2-tetracarbonitrile

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**Abstract**—Hydrolysis of 6,6-dimethyl-4,8-dioxo-5,7-dioxaspiro[2.5]octane-1,1,2,2-tetracarbonitrile in aqueous dioxane in the presence of hydrogen bromide gave a mixture of 2,2,3,3-tetracyanocyclopropane-1-carboxylic acid and ammonium 3-cyano-4-dicyanomethylidene-5-oxo-4,5-dihydro-1*H*-pyrrol-2-olate. Hydrolysis of the same compound in the presence of sulfuric acid was accompanied by nitrogen migration and led to the formation of (1*R**,2*S**,3*S**)-1,3-dicyanocyclopropane-1,2-dicarboxamide whose structure was proved by X-ray analysis.

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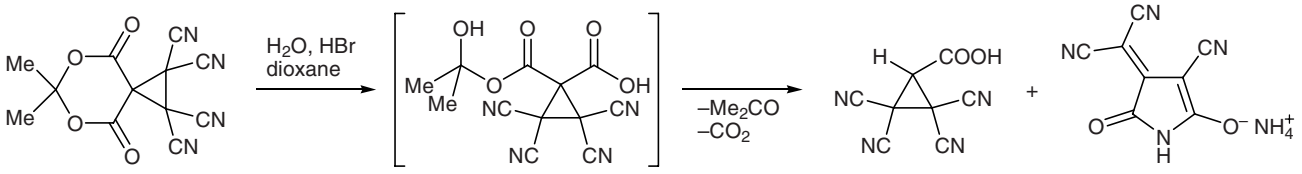
We previously reported that tetracyanoethylene reacts with monobromo derivative of Meldrum's acid to give, depending on the conditions, 6,6-dimethyl-4,8-dioxo-5,7-dioxaspiro[2.5]octane-1,1,2,2-tetracarbonitrile (**I**) or 2,2,3,3-tetracyanocyclopropane-1-carboxylic acid (**II**) [1]. Reactions of the latter with iodides lead to the corresponding 3-cyano-4-dicyanomethylidene-5-oxo-4,5-dihydro-1*H*-pyrrol-2-olates [2]. Studies on the relations between the crystalline structure and crystal packing and the nature of cation in these salts are now in progress; some results were reported in [3–6]. Acid **II** is the key initial compound for their synthesis. However, the procedure described in [1] ensures relatively poor yield of **II**. Therefore, in the present work we examined the hydrolysis of spirocyclic compound **I** in more detail.

Previous studies on the hydrolysis of some polycyanocyclopropanes showed that transformations of the cyano groups therein can be accompanied by opening of the three-membered ring or not. For example, treatment of 3,3-dimethylcyclopropane-1,1,2,2-tetracarbonitrile with alkali in aqueous methanol (reaction time 3 h) smoothly afforded 5-carbamoyl-6,6-dimethyl-2,4-dioxo-3-azabicyclo[3.1.0]hexane-1-carboxylic acid which is very stable to subsequent hydrolysis [7]. Likewise, hydrolysis of pentacyanocyclopropanecarboxylic acid esters and amides in the presence of sulfuric acid does not involve the three-membered ring, and the product is dicyanocyclopropanecarboxamide [8]. Processes accompanied by opening of the cyclopropane ring were described in [9, 10]. Heating of tetracyanocyclopropanes in boiling concentrated hydrochloric acid gives derivatives of itaconic acid.

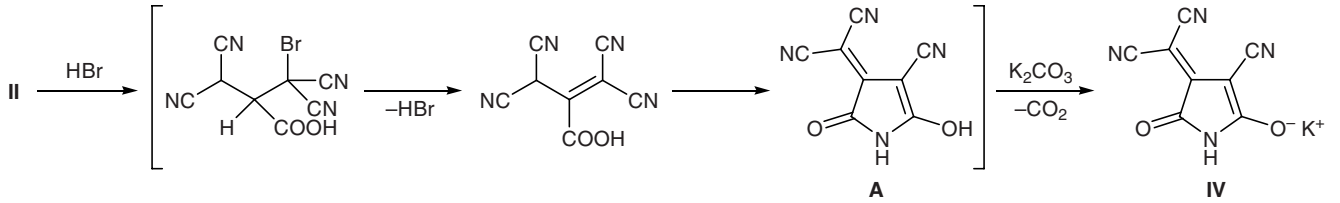
We found that the reaction of compound **I** with hydrobromic acid in dioxane in 3 h gives about 10% of acid **II** which crystallizes from the reaction mixture (Scheme 1). Increase of the reaction time leads to reduced yield. When the yellow filtrate obtained after

**Scheme 1.**




**I** **II** **III**

**Scheme 2.**




separation of acid **II** was neutralized with potassium carbonate, we isolated potassium 3-cyano-4-dicyanomethylidene-5-oxo-4,5-dihydro-1*H*-pyrrol-2-olate (**IV**). We presumed that the process is accompanied by isomerization of **II** into acid **A** (Scheme 2). This transformation may be rationalized assuming nucleophilic catalysis by hydrobromic acid. However, we failed to isolate acid **A** as individual substance. Evaporation of the reaction mixture gave salt **III** and ammonium bromide. The source of ammonium in the reaction mixture may be only cyano groups in molecule **I**, i.e., the reactions shown in Schemes 1 and 2 are accompanied by hydrolysis of the cyano groups. Hydrolysis of the latter may be promoted by both acid and nucleophilic catalysis.

In order to exclude nucleophilic catalysis by bromide ion, the hydrolysis of **I** was performed in the presence of less nucleophilic sulfuric acid. In this case, the reaction took a different path, and the product was (1*R**,2*S**,3*S**)-1,3-dicyanocyclopropane-1,2-dicarboxamide (**V**) (yield 60%). Scheme 3 shows a possible mechanism of formation of one enantiomer of **V**. The molecular and crystalline structures of diamide **V** were studied by X-ray analysis (Fig. 1). A suitable single crystal was obtained by slow evaporation of an aqueous solution. It was found that four hydrogen atoms in the amide group, as well as hydrogen atoms in solvate water molecules, are involved in hydrogen bonding, giving rise to double chains of molecules along the crystallographic *b* axis (Fig. 2). Here, the neighboring chains are linked to each other through water molecules to form a two-dimensional structure, while interactions between the cyano groups [11] lead to formation of 3D-molecular structure in crystal.

Taking into account mutual arrangement of the carboxamide and cyano groups in molecule **V**, we presumed that the reaction involves intramolecular migration of nitrogen atom (Scheme 3). In the first step acid **II** is likely to be formed. This assumption is supported by the fact that the hydrolysis of acid **II** (prepared by a different method) in 10% $H_2SO_4$ gives 65% of diamide **V**. Probably, the subsequent hydrolysis involves assistance by the carboxy group (since only the cyano groups in the *cis* position with respect to the carboxy group are transformed) with formation of diamido acid **E** through a series of intermediates, including furans **B** and **D** and amido acid **C**. Acid **E** could give rise to equilibrium with isomeric diamido

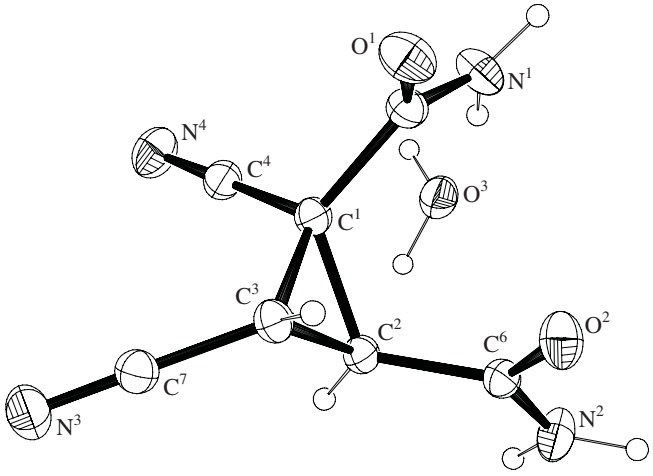



**Fig. 1.** Structure of the molecule of (1*R**,2*S**,3*S**)-1,3-dicyanocyclopropane-1,2-dicarboxamide (**V**) according to the X-ray diffraction data.

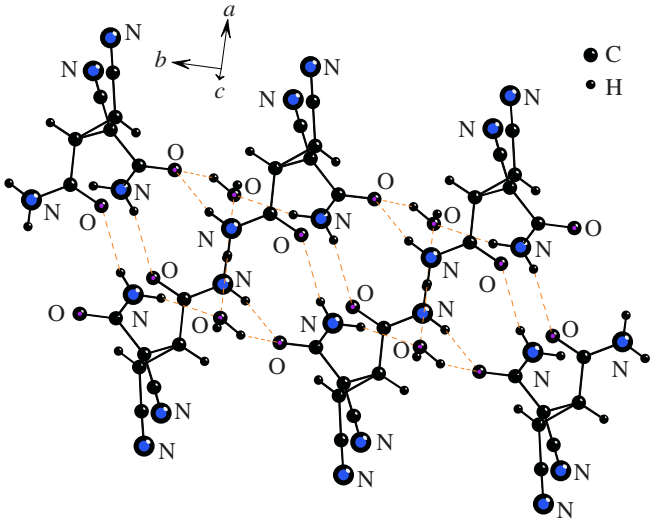
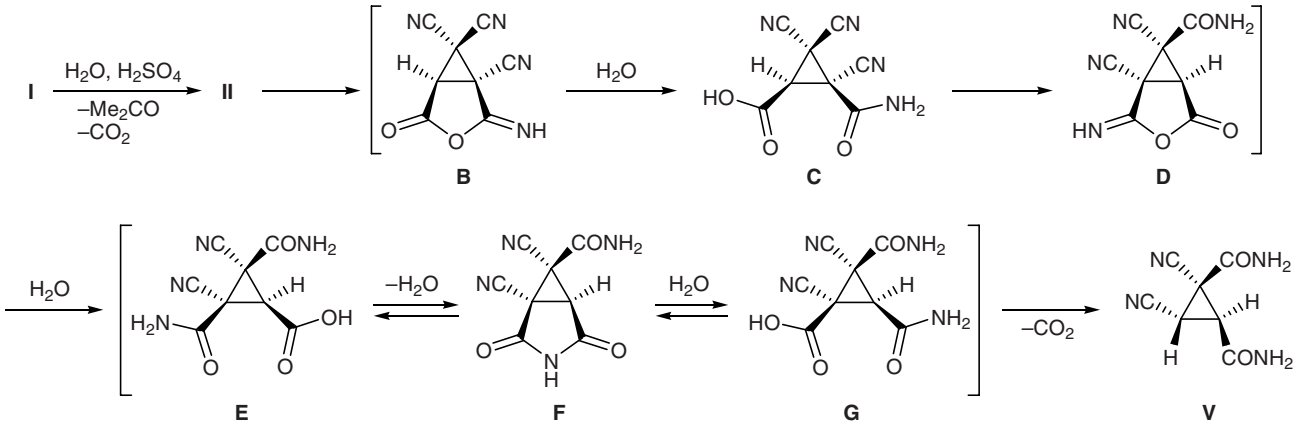



**Fig. 2.** Double-chain hydrogen bond system formed by molecules **V** in crystal.

**Scheme 3.**



acid **G** through cyclic imide **F** with participation of water. Decarboxylation of acid **G** shifts the equilibrium toward the final product, diamide **V**.

## EXPERIMENTAL

The progress of reactions and the purity of products were monitored by TLC on Silufol UV-254 plates (spots were visualized by UV irradiation, treatment with iodine vapor, or thermal treatment). The IR spectra were recorded on an FSM 1201 instrument from samples dispersed in mineral oil. The $^1$H NMR spectrum was measured on a Bruker AM-500 spectrometer at a frequency of 500.13 MHz. The X-ray diffraction data for a single crystal of compound **V** were acquired on an Enraf–Nonius CAD-4 four-circle automatic diffractometer (Cu$K_\alpha$ irradiation, graphite monochromator, ω-scanning).

**2,2,3,3-Tetracyanocyclopropane-1-carboxylic acid (II).** Nitrile **I**, 5.4 g (0.02 mol), was dissolved in 20 ml of dioxane, 20 ml of 10% hydrobromic acid was added, water was then added until the mixture turned turbid, and the mixture was left to stand for 3 h at 6°C. The curdy precipitate was filtered off, washed with water, and dried first between filter paper sheets and then in a desiccator over $P_2O_5$. Yield 0.37 g (10%), mp 132–134°C (decomp.); published data [1]: mp 134–136°C (decomp.).

**Ammonium 3-cyano-4-dicyanomethylidene-5-oxo-4,5-dihydro-1*H*-pyrrol-2-olate (III).** The filtrate obtained after separation of compound **II** was left to stand until complete evaporation of the solvent. Water, 20 ml, was added to the residue, the mixture was stirred, the tarry material was filtered off, and the filtrate was left to stand allowing water to evaporate. Initially, orange–red crystals of salt **III** separated, and then colorless crystals of ammonium bromide precipitated. The orange–red crystals were filtered off before crystallization of ammonium bromide and dissolved in 10 ml of water, and the solution was treated with charcoal and left to stand for 24 h. The solution was filtered, and the filtrate was evaporated to dryness. Yield 1.00 g (25%), orange needles, mp 170–175°C (decomp.); published data [6]: mp 175°C (decomp.).

**Potassium 3-cyano-4-dicyanomethylidene-5-oxo-4,5-dihydro-1*H*-pyrrol-2-olate (IV).** The filtrate obtained after separation of compound **II** (see above) was treated with solid potassium carbonate until carbon dioxide no longer evolved. The orange precipitate was filtered off and dried in air. Yield 1.34 g (30%), mp 185°C (decomp.) [3].

**(1*R**,2*S**,3*S**)-1,3-Dicyanocyclopropane-1,2-dicarboxamide (V).** *a*. Nitrile **I**, 5.4 g (0.02 mol), was added to 50 ml of 10% sulfuric acid, and the mixture was heated under stirring until it became homogeneous. The mixture was filtered, the filtrate was left to stand for 3 days, and the precipitate was filtered off, washed with water and cold diethyl ether, and dried in air. Yield 2.1 g (60%), mp 140°C (decomp., from $H_2O$). IR spectrum, ν, cm$^{-1}$: 3040 (C–H), 2260 (C≡N), 1700 (C=O). $^1$H NMR spectrum (DMSO-$d_6$), δ, ppm: 4.2 d (1H, CH), 3.7 d (1H, CH), 8.0 s (1H, $CONH_2$), 7.7 s (1H, $CONH_2$), 7.4 s (1H, $CONH_2$), 7.8 s (1H, $CONH_2$). Found, %: C 43.05; H 4.05; N 28.70. $C_7H_6N_4O_2\cdot H_2O$. Calculated, %: C 42.86; H 4.11; N 28.56. Crystallographic parameters: $a$ = 10.8713(14), $b$ = 6.3701(5), $c$ = 13.3035(14) Å; β = 106.11(1)°; $V$ = 885.09(1) Å$^3$; $Z$ = 4, space group $P2_1/c$ (monoclinic crystal system). The positions of non-hydrogen atoms were refined in full-matrix anisotropic approximation using 1767 reflections acquired in the range $2\theta < 144°$. Hydrogen atoms were localized from the Fourier difference

syntheses, and their positions were refined in isotropic approximation. The divergence factor $R$ was 0.038 [from 1547 reflections with $F^2 > 4\sigma(F^2)$]. The complete set of crystallographic data was deposited to the Cambridge Crystallographic Data Center (entry no. CCDC 295882).

*b*. Compound **V** was synthesized in a similar way from 0.93 g (5 mmol) of 2,2,3,3-tetracyanocyclopropane-1-carboxylic acid. Yield 0.58 g (65%).

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