

# Reaction of 2,2,3,3-Tetracyanocyclopropanecarboxylic Acid with Iodides. Synthesis of 3-Cyano-4-dicyanomethylidene-5-oxo-4,5-dihydro-1*H*-pyrrol-2-olates

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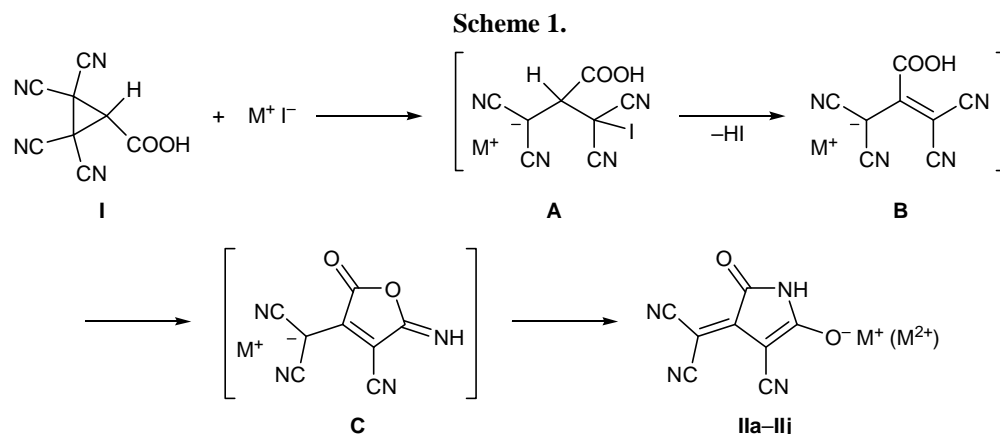
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**Abstract**—Reactions of 2,2,3,3-tetracyanocyclopropanecarboxylic acid with potassium, sodium, calcium, strontium, barium, ammonium, *N*-methylpyridinium, *N*-methylquinolinium, *N,N*-dimethyl-1,4-diazabicyclo[2.2.2]octane-1,4-dium, and *N,N*-dimethylanilinium iodides afforded the corresponding 3-cyano-4-dicyanomethylidene-5-oxo-4,5-dihydro-1*H*-pyrrol-2-olates.

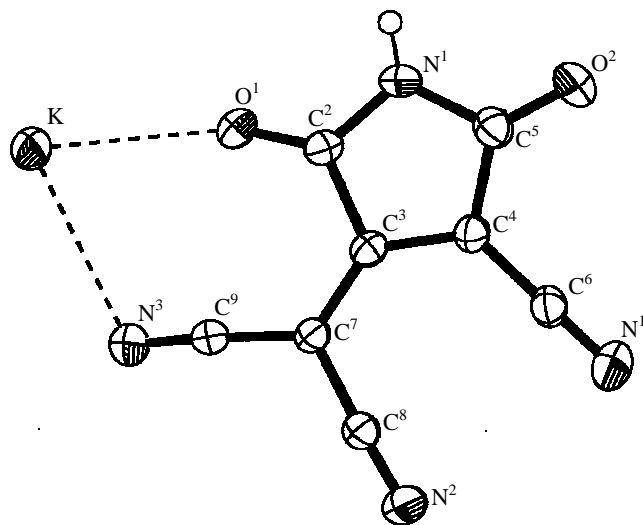
It is known that compounds containing a cyclopropane ring generally do not undergo ring opening by the action of nucleophiles. Exceptions are cyclopropane derivatives having five or six electron-acceptor groups. Such compounds are readily opened by the action of soft nucleophiles, the best of which is likely to be iodide ion. The structure of products formed in reactions with iodides depends on both substrate nature and nucleophilic power of the cation. Potassium iodide and aliphatic amine hydroiodides usually give rise to the corresponding propenides and cyanogen iodide [1, 2]. If the cation exhibits nucleophilic properties, e.g., as in aniline hydroiodide, the

reaction follows a more complicated pattern, and the products are tricyanovinyl [1, 3, 4] or dicyanomethylidene derivatives [4], depending on the substituent nature in the initial cyclopropane.

We recently reported on the synthesis of 2,3,3,3-tetracyanocyclopropanecarboxylic acid (**I**) [5]. This compound very readily reacts with potassium iodide in aqueous dioxane to give 53% of potassium 3-cyano-4-dicyanomethylidene-5-oxo-4,5-dihydro-1*H*-pyrrol-2-olate (**IIa**). Presumably, initial attack by iodide ion on the substrate gives substituted propanide **A** which then loses hydrogen iodide molecule with formation of propenide **B**. Intramolecular cyclization of the latter



$M^+$  ( $M^{2+}$ ) =  $K^+$  (**a**),  $Na^+$  (**b**),  $Ca^{2+}$  (**c**),  $Sr^{2+}$  (**d**),  $Ba^{2+}$  (**e**),  $NH_4^+$  (**f**), 1-methylpyridinium (**g**), *N,N*-dimethylanilinium (**h**), 1-methylquinolinium (**i**), 1,4-dimethyl-1,4-diazabicyclo[2.2.2]octane-1,4-dium (**j**).



Structure of the molecule of potassium 3-cyano-4-dicyanomethylidene-5-oxo-4,5-dihydro-1*H*-pyrrol-2-olate (**IIa**) according to the X-ray diffraction data.

leads to furan derivative **C** which undergoes rearrangement into more stable anion **II**. The structure of potassium salt **IIa** was determined by X-ray analysis of a single crystal (see figure). All outer heteroatoms in the anion of salt **IIa** in crystal form a polyhedron surrounding the cation, and the anions are linked by hydrogen bonds to produce channels which localize the cations [6]. Single crystals with such a structure may possess useful electronic and optoelectronic properties. With a view to elucidate the effect of the cation structure on crystal packing we synthesized 3-cyano-4-dicyanomethylidene-5-oxo-4,5-dihydro-1*H*-pyrrol-2-olate salts with various organic and inorganic anions directly by reaction of acid **I** with the corresponding iodides. Apart from alkali and alkaline-earth metal cations and their organic analogs, it was interesting to involve organic cations capable of  $\pi$ - $\pi$  stacking, as well as *d*-element cations capable of forming chelate structures [7].

The following relations were found while synthesizing salts **IIa–IIj**. Carboxylic acid **I** is converted into salt **II** only by the action of free iodide ion: no reaction occurred with covalent silver and lead iodides even on heating in boiling dimethylformamide. The formation of the corresponding salts from both ammonium iodide and *N,N*-dimethylanilinium iodide indicates that nucleophilicity of the cation is not significant in the reaction under study. The reaction is accompanied by liberation of hydrogen iodide; therefore, equilibrium is likely to establish during the process; the position of this equilibrium depends on the solvent. Liberated

hydrogen iodide partially decomposes to release molecular iodine which can contaminate the target product. The yield of the latter depends on the solubility of the initial iodide and final salt **II**. The best results were obtained using aqueous dioxane or aqueous alcohol as solvent. When the solubilities of the iodide and the corresponding salt **II** differed insignificantly, the reaction equilibrium can be displaced taking advantage of volatility of hydrogen iodide and its reducing ability.

The crystal structures of salts **IIg** and **IIj** were examined by the X-ray diffraction method. The results showed radically different modes of crystal packing in these salts [7, 8], which suggests prospects in continuing studies in this line.

## EXPERIMENTAL

The IR spectra were recorded on a UR-20 spectrometer from samples dispersed in mineral oil. The purity of the products was checked by TLC on Silufol UV-254 plates.

**Potassium 3-cyano-4-dicyanomethylidene-5-oxo-4,5-dihydro-1*H*-pyrrol-2-olate (IIa).** A solution of 0.166 g (0.001 mol) of potassium iodide in 3 ml of water was added in one portion to a suspension of 0.186 g (0.001 mol) of tetracyanocyclopropanecarboxylic acid **I** in 3 ml of 1,4-dioxane. The mixture was stirred for 5 min, and it initially turned dark red and transparent, and then a yellow solid separated. The mixture was kept for 2 h at 5°C, and the precipitate was filtered off, washed with cold isopropyl alcohol, and dried in a vacuum desiccator. Yield 0.119 g (53%), decomposition point 185°C (from water). IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 3300 (NH); 2210, 2230 (CN); 1720 (C=O). Found, %: C 42.89; H 0.41; N 25.02. Calculated, %: C 42.85; H 0.45; N 24.99.

**Sodium 3-cyano-4-dicyanomethylidene-5-oxo-4,5-dihydro-1*H*-pyrrol-2-olate (IIb)** was synthesized in a similar way. Yield 0.116 g (56%), decomposition point 220°C (from water). IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 3280 (NH); 2210, 2230 (CN); 1725 (C=O). Found, %: C 46.20; H 0.52; N 26.87. Calculated, %: C 46.17; H 0.48; N 26.92.

**Calcium 3-cyano-4-dicyanomethylidene-5-oxo-4,5-dihydro-1*H*-pyrrol-2-olate (IIc).** A solution of 0.085 g (0.0005 mol) of calcium iodide in 3 ml of water was added in one portion to a suspension of 0.186 g (0.001 mol) of tetracyanocyclopropanecarboxylic acid **I** in 3 ml of isopropyl alcohol. After stirring for 5 min, the mixture turned red-brown and transparent. The solvent was evaporated at 40–45°C

until crystals began to separate from the solution, the mixture was cooled, and the yellow crystals were filtered off, washed in succession with small portions of cold 1,4-dioxane and diethyl ether, and dried in a vacuum desiccator. Yield 0.185 g (45%), decomposition point 215°C. IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 3290 (NH); 2215, 2225 (CN); 1725 (C=O). Found, %: C 46.86; H 0.52; N 27.30. Calculated, %: C 46.83; H 0.49; N 27.31.

**Strontium 3-cyano-4-dicyanomethylidene-5-oxo-4,5-dihydro-1H-pyrrol-2-olate (II<sub>d</sub>)** was synthesized in a similar way. Yield 0.174 g (38%), decomposition point 210°C. IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 3300 (NH); 2210, 2220 (CN); 1720 (C=O). Found, %: C 41.96; H 0.48; N 24.41. Calculated, %: C 41.97; H 0.44; N 24.47.

**Barium 3-cyano-4-dicyanomethylidene-5-oxo-4,5-dihydro-1H-pyrrol-2-olate (II<sub>e</sub>)**. A solution of 0.132 g (0.0005 mol) of barium iodide in 3 ml of water was added in one portion to a suspension of 0.186 g (0.001 mol) of tetracyanocyclopropanecarboxylic acid **I** in 3 ml of isopropyl alcohol. After stirring for 5 min, the mixture turned red-brown and transparent. The mixture was then stirred for 15–20 min until crystals began to separate from the solution. The mixture was cooled, and the yellow crystals were filtered off, washed in succession with small portions of cold 1,4-dioxane and diethyl ether, and dried in a vacuum desiccator. Yield 0.330 g (65%), decomposition point 200°C. IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 3320 (NH); 2230, 2220 (CN); 1720 (C=O). Found, %: C 37.83; H 0.43; N 22.12. Calculated, %: C 37.86; H 0.40; N 22.08.

**Ammonium 3-cyano-4-dicyanomethylidene-5-oxo-4,5-dihydro-1H-pyrrol-2-olate (II<sub>f</sub>)**. A solution of 0.144 g (0.001 mol) of ammonium iodide in 3 ml of water was added in one portion to a suspension of 0.186 g (0.001 mol) of tetracyanocyclopropanecarboxylic acid **I** in 3 ml of isopropyl alcohol. The mixture was stirred for 5 min, and it turned dark red and transparent. The mixture was evaporated at 40–45°C almost to dryness, the residue was washed with diethyl ether in 2-ml portions to remove iodine, 2 ml of aqueous isopropyl alcohol (1:1) was added to the residue, and the mixture was thoroughly ground. The yellow crystals were filtered off, washed in succession with small portions of cold isopropyl alcohol and 1,4-dioxane, and dried in a vacuum desiccator. Yield 0.095 g (47%), decomposition point 175°C (from aqueous isopropyl alcohol). IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 3270 (NH); 2720 ( $\text{NH}_4^+$ ); 2220, 2230 (CN); 1720 (C=O). Found, %: C 47.34; H 2.52; N 34.48. Calculated, %: C 47.30; H 2.48; N 34.47.

**N-Methylpyridinium 3-cyano-4-dicyanomethylidene-5-oxo-4,5-dihydro-1H-pyrrol-2-olate (II<sub>g</sub>)**. A solution of 0.221 g (0.001 mol) of *N*-methylpyridinium iodide in 3 ml of water was added in one portion to a suspension of 0.186 g (0.001 mol) of tetracyanocyclopropanecarboxylic acid **I** in 3 ml of isopropyl alcohol. The mixture quickly turned red-brown and homogeneous, and a voluminous solid began to precipitate almost immediately. The mixture was stirred for 15–20 min and cooled, and the orange-yellow crystals were filtered off, washed with a small amount of cold aqueous isopropyl alcohol (1:1), and dried in a vacuum desiccator. Yield 0.153 g (55%), decomposition point 205°C (from 1,4-dioxane). IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 3300 (NH); 2230, 2210 (CN); 1730 (C=O). Found, %: C 60.18; H 3.29; N 25.05. Calculated, %: C 60.21; H 3.25; N 25.08.

**N,N-Dimethylanilinium 3-cyano-4-dicyanomethylidene-5-oxo-4,5-dihydro-1H-pyrrol-2-olate (II<sub>h</sub>)** was synthesized in a similar way. Yield 0.153 g (55%), decomposition point 222°C (from aqueous isopropyl alcohol, 1:1). IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 3330 (NH); 2230, 2215 (CN); 1720 (C=O). Found, %: C 62.50; H 4.29; N 22.73. Calculated, %: C 62.53; H 4.26; N 22.79.

**N-Methylquinolinium 3-cyano-4-dicyanomethylidene-5-oxo-4,5-dihydro-1H-pyrrol-2-olate (II<sub>i</sub>)** was synthesized in a similar way. Yield 0.153 g (55%), light yellow fibrous crystals, decomposition point 235°C (from aqueous isopropyl alcohol). IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 3340 (NH); 2225, 2210 (CN); 1725 (C=O). Found, %: C 65.62; H 3.40; N 21.23. Calculated, %: C 65.65; H 3.37; N 21.27.

**1,4-Dimethyl-1,4-diazabicyclo[2.2.2]octane-1,4-dium 3-cyano-4-dicyanomethylidene-5-oxo-4,5-dihydro-1H-pyrrol-2-olate (II<sub>j</sub>)**. A solution of 0.093 g (0.0005 mol) of 1,4-dimethyl-1,4-diazabicyclo[2.2.2]-octane-1,4-dium diiodide in 3 ml of water was added in one portion to a suspension of 0.186 g (0.001 mol) of tetracyanocyclopropanecarboxylic acid **I** in 3 ml of isopropyl alcohol. The mixture was stirred, and it turned red-brown and homogeneous. After stirring for 20–30 min, a dark red finely crystalline solid precipitated. The mixture was cooled, the precipitate was filtered off and dissolved in 10 ml of water, and the solution was heated for several minutes at the boiling point until violet iodine vapor no longer evolved. The resulting yellow solution was cooled, and the yellow-orange needles were filtered off, washed with cold aqueous isopropyl alcohol (1:1), and dried in a vacuum desiccator. Yield 0.128 g (25%), decomposition

point 225°C. IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 3320 (NH); 2230, 2210 (CN); 1720 (C=O). Found, %: C 56.28; H 3.89; N 27.38. Calculated, %: C 56.25; H 3.93; N 27.33.

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