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SHORT COMMUNICATIONS

Reaction of Tetracyanoethylene with 1,2-Cyclohexanedione and Bis(cyclohexanon-2-yl)methane

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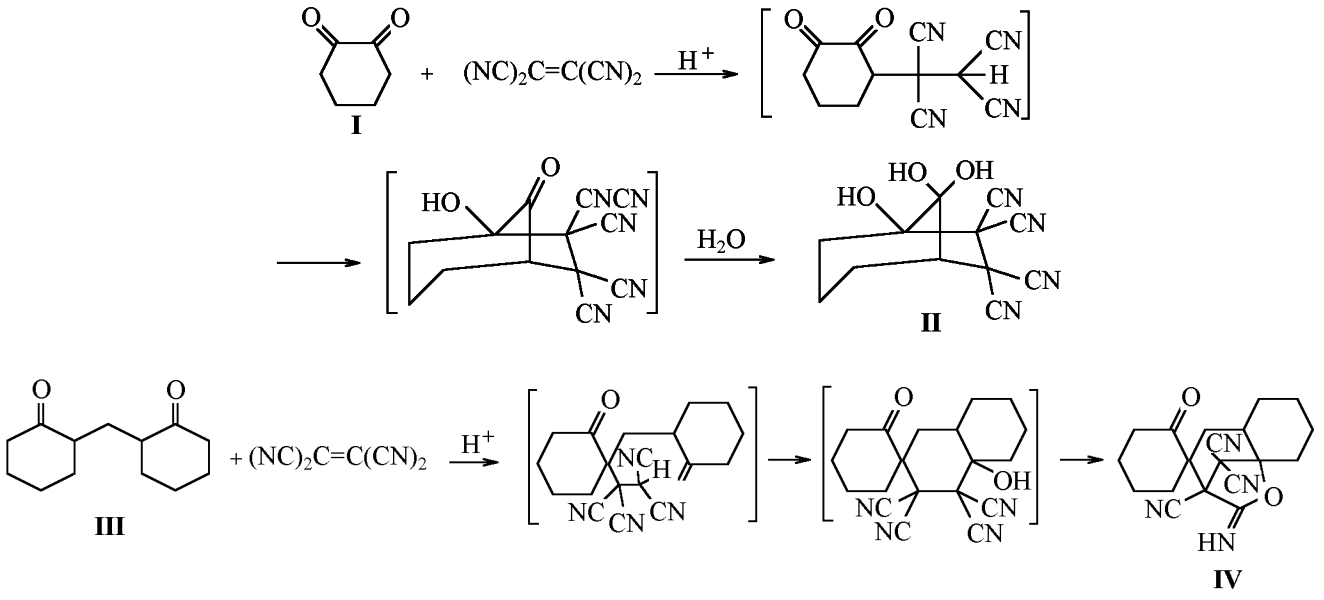
The first study on reactions between tetracyanoethylene and carbonyl compounds was published in 1957 [1]. We extended the investigations in this field and established that the arising β,β,γ,γ-tetracyanoalkanones were very reactive [2, 3]. However in this process were involved only some β-dicarbonyl compounds whose addition to tetracyanoethylene followed by cyclization due to interactions NH^CN and OH^CN resulted in formation of pyrroles, furans, and pyrans [4].

We found that the reaction between tetracyanoethylene and 1,2 -cyclohexanedione (**I**) and bis(cyclohexanon-2-yl)methane (**III**) gave rise respectively to 6,6,7,7-tetracyanobicyclo[3.2.1]octane-1,8,8-triol (**II**) and 7-imino-2-spiro-1'-[2'-oxocyclohexane]-4,5-tetramethylene-6-oxabicyclo[3.2.1]octane-1,8,8-tricarbonitrile (**IV**). The main distinction of these reactions from those with β-dicarbonyl compounds consisted in interaction of the acid fragment $CH(CN)_2$ with the carbonyl group resulting in formation of a cycloalkane ring.

In reaction of tetracyanoethylene with diketone **I** occurs unusual 1,3-cycloaddition to afford hydrate **II**, and with diketone **III** proceeds 1,4-cycloaddition to furnish hydrofuran **IV**.

The structure of compounds **II** and **IV** was determined by X-ray diffraction study.

6,6,7,7-Tetracyanobicyclo[3.2.1]octane-1,8,8-triol (II). To 1.28 g (0.01 mol) of tetracyanoethylene in 20 ml of dioxane was added 1.12 g (0.01 mol) of 1,2-cyclohexanedione and 5–6 drops of concn. HCl. In 24 h precipitate separated that was filtered off, washed with 2-propanol and ether. Yield 81%. mp 130–131°C. IR spectrum: 2260, 2270, 3100–3300 cm^{-1}. X-Ray analysis data: space group $P2_1/C$ at –90°C, *a* 11.356(4), *b* 8.596(3),



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c 19.225(6) Å, α 90°, β 90.73(3)°, γ 90°, *V* 1877(1) Å^3, *Z* 4, *R* 0.045.

7-Imino-2-spiro-1′-[2′-oxocyclohexane]-4,5-tetramethylene-6-oxabicyclo[3.2.1]octane-1,8,8-tricarbonitrile (IV). To 1.28 g (0.01 mol) of tetracyanoethylene in 20 ml of dioxane was added 2.08 g (0.01 mol) of bis(cyclohexanon-2-yl)methane and 3–4 drops of conc. HCl. After 12 h was added 50 ml of water. separated a precipitate that was filtered off, washed with 2-propanol and ether. Yield 85%. mp 218–219°C. IR spectrum: 1700, 2260, 3280 cm^{-1}. X-Ray analysis data: space group $R2_1/S$ at –90°C, *a* 8.932(2), *b* 10.008(5), *c* 19.404(3) Å, α 90°, β 93.56 (10)°, γ 90°, *V* 1731.2(10) Å^3, *Z* 4, *R* 0.0436.

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