

SHORT
COMMUNICATIONS

Decyanation of 5-Alkyl-6-aryl-4-oxocyclohexane-1,1,2,2-tetracarbonitriles

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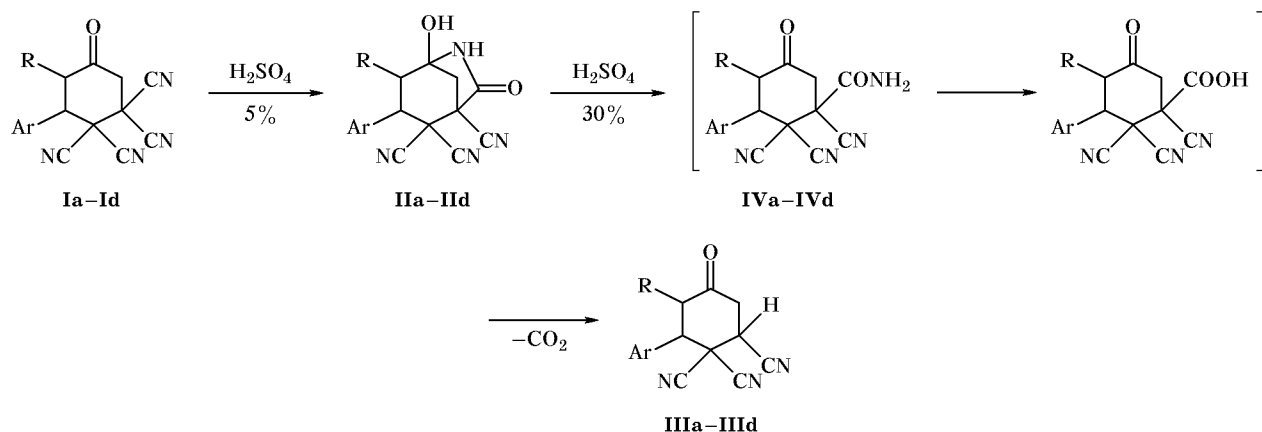
4-Oxocyclohexane-1,1,2,2-tetracarbonitriles are formed by reaction of tetracyanoethylene with α,β -unsaturated ketones [1, 2]. By the action of water they are converted into 5-hydroxy-7-oxo-6-azabicyclo[3.2.1]octane-1,2,2-tricarbonitriles. We have revealed unusual decyanation of tetracyanocyclohexanones **Ia–Id** to tricyanocyclohexanones **IIIa–IIIId** in the presence of sulfuric acid. This is the first example of selective elimination of only one cyano group in the series of polycyanoalkanes, which occurs in acid medium. Analogous known reactions require the presence of reducing agents [3, 4]. Selective decyanation of one cyano group in position 2 is explained by its intramolecular interaction with the carbonyl group. We have also found that such interaction gives rise to 5-hydroxy-7-oxo-6-azabicyclo[3.2.1]octane-1,2,2-tricarbonitriles **IIa–IIId** not only by the action of water on cyclohexanones **Ia–Id** [1] but also on heating of compounds **I** with 5% aqueous sulfuric acid. Treatment of **Ia–Id** with H_2SO_4 under more severe condi-

tions leads to formation of tricyanocyclohexanones **IIIa–IIIId** (Scheme 1).

That the transformation **I**→**III** involves intermediate formation of azabicyclooctanes **IIa–IIId** was confirmed by the conversion of compounds **II** into **III**. Intermediates **IVa–IVd** shown in Scheme 1 are formed via retro-cyclization of **IIa–IIId**, which was described by us previously [1]. Hydrolysis of amides **IVa–IVd** and subsequent decarboxylation of the corresponding carboxylic acids yield the final products, tricyanocyclohexanones **IIIa–IIIId**.

5-Hydroxy-4-methyl-7-oxo-3-phenyl-6-azabicyclo[3.2.1]octane-1,2,2-tricarbonitrile (IIa). Tetracyanocyclohexanone **Ia**, 0.01 mol, was dissolved in a mixture of 5 ml of dioxane and 5 ml of 5% sulfuric acid, and the solution was heated for 10 min under reflux. The mixture was diluted with 50 ml of water, and the precipitate was filtered off, washed with water, 2-propanol, and diethyl ether, and dried in

Scheme 1.



I–IV, R = Me (**a**, **c**), Pr (**b**, **d**); Ar = Ph (**a**, **b**), $MeOC_6H_4$ (**c**, **d**).

air. Yield 91%, mp 223–224°C (decomp.; from 2-propanol). IR spectrum, ν , cm^{-1} : 3525 (OH); 3340, 1615 (NH); 2270 ($\text{C}\equiv\text{N}$); 1705 ($\text{C}=\text{O}$).

Compounds **IIb–IIc** were synthesized and purified in a similar way.

5-Hydroxy-7-oxo-3-phenyl-4-propyl-6-azabicyclo[3.2.1]octane-1,2,2-tricarbonitrile (IIb). Yield 95%, mp 211–212°C (decomp.; from 2-propanol). IR spectrum, ν , cm^{-1} : 3535 (OH); 3335, 1645 (NH); 2270 ($\text{C}\equiv\text{N}$); 1710 ($\text{C}=\text{O}$).

5-Hydroxy-3-*p*-methoxyphenyl-4-methyl-7-oxo-6-azabicyclo[3.2.1]octane-1,2,2-tricarbonitrile (IIc). Yield 95%, mp 228–229°C (decomp.; 2-propanol). IR spectrum, ν , cm^{-1} : 3450 (OH); 3330, 1625 (NH); 2280 ($\text{C}\equiv\text{N}$); 1710 ($\text{C}=\text{O}$).

5-Hydroxy-3-*p*-methoxyphenyl-7-oxo-4-propyl-6-azabicyclo[3.2.1]octane-1,2,2-tricarbonitrile (IIc). Yield 95%, mp 185–186°C (decomp.; from *i*-PrOH). IR spectrum, ν , cm^{-1} : 3510 (OH); 3350, 1645 (NH); 2275 ($\text{C}\equiv\text{N}$); 1710 ($\text{C}=\text{O}$).

5-Methyl-4-oxo-6-phenylcyclohexane-1,1,2-tricarbonitrile (IIIa). To a solution of 0.01 mol of tetracyanocyclohexanone **Ia** or azabicyclooctane **IIa** in 5 ml of dioxane we added under continuous stirring 5 ml of 30% sulfuric acid. The mixture was heated for 24–48 h under reflux and diluted with 50 ml of water, and the precipitate was filtered off, washed with water and 2-propanol, and dried in air. Yield 76%, mp 165–166°C (from 2-propanol). IR spectrum, ν , cm^{-1} : 2265 ($\text{C}\equiv\text{N}$), 1710 ($\text{C}=\text{O}$). ^1H NMR spectrum (DMSO- d_6), δ , ppm: 7.51–7.22 m (5H, Ph), 4.6 d.d (1H, CHCN, $J = 15.0, 6.5$ Hz), 3.85 d (1H, CHAr, $J = 14.0$ Hz), 3.47 m (1H, CHMe), 3.12 d.d (1H, COCH₂, $J = 15.0, 6.5$ Hz), 3.01 t (1H, COCH₂, $J = 15.0$ Hz), 0.82 d (3H, CH₃, $J = 6.5$ Hz). Mass spectrum, m/z : M^+ 263. Found, %: C 73.02; H 4.91; N 15.92. $\text{C}_{16}\text{H}_{13}\text{N}_3\text{O}$. Calculated, %: C 72.99; H 4.98; N 15.96. Compounds **IIIb–IIIc** were synthesized in a similar way.

4-Oxo-6-phenyl-5-propylcyclohexane-1,1,2-tricarbonitrile (IIIb). Yield 81%, mp 176–177°C (from 2-propanol). IR spectrum, ν , cm^{-1} : 2270 ($\text{C}\equiv\text{N}$), 1705 ($\text{C}=\text{O}$). ^1H NMR spectrum (DMSO- d_6), δ , ppm: 7.48–7.21 m (5H, Ph), 4.44 d.d (1H, CHCN, $J = 13.0, 5.5$ Hz), 3.81 d (1H, CHAr, $J = 14.0$ Hz), 3.47 d.t (1H, CHPr, $J = 14.0, 6.5$ Hz), 3.09 d.d (1H, COCH₂, $J = 13.0, 4.5$ Hz), 2.95 t (1H, COCH₂, $J = 13.0$ Hz), 1.35–1.0 m (4H, CH₂CH₂CH₃), 0.81 d (3H, CH₃, $J = 6.8$ Hz). Mass spectrum, m/z : M^+ 291. Found, %:

C 69.72; H 5.12; N 14.35. $\text{C}_{17}\text{H}_{15}\text{N}_3\text{O}_2$. Calculated, %: C 69.61; H 5.15; N 14.33.

6-*p*-Methoxyphenyl-5-methyl-4-oxocyclohexane-1,1,2-tricarbonitrile (IIIc). Yield 79%, mp 168–169°C (from 2-propanol). IR spectrum, ν , cm^{-1} : 2270, 2265 ($\text{C}\equiv\text{N}$); 1705 ($\text{C}=\text{O}$). ^1H NMR spectrum (DMSO- d_6), δ , ppm: 7.36 d (2H, *o*-H, $J = 8.5$ Hz), 7.03 d (2H, *m*-H, $J = 8.5$ Hz), 4.66 d.d (1H, CHCN, $J = 15.0, 6.5$ Hz), 3.83 s (3H, OCH₃), 3.74 d (1H, CHAr, $J = 14.0$ Hz), 3.21 d.q (1H, CHMe, $J = 14.0, 6.5$ Hz), 3.07 d.d (1H, COCH₂, $J = 15.0, 4.5$ Hz), 2.99 t (1H, COCH₂, $J = 15.0$ Hz), 0.78 d (3H, CH₃, $J = 6.5$ Hz). Mass spectrum, m/z : M^+ 293. Found, %: C 69.72; H 5.12; N 14.35. $\text{C}_{17}\text{H}_{15}\text{N}_3\text{O}_2$. Calculated, %: C 69.61; H 5.15; N 14.33.

6-*p*-Methoxyphenyl-5-propyl-4-oxocyclohexane-1,1,2-tricarbonitrile (IIIc). Yield 71%, mp 171–172°C (from 2-propanol). IR spectrum, ν , cm^{-1} : 2270 ($\text{C}\equiv\text{N}$); 1710 ($\text{C}=\text{O}$). ^1H NMR spectrum (DMSO- d_6), δ , ppm: 7.49 d (2H, *o*-H, $J = 8.5$ Hz), 7.1 d (2H, *m*-H, $J = 8.5$ Hz), 4.48 d.d (1H, CHCN, $J = 15.0, 6.5$ Hz), 3.83 s (3H, OCH₃), 3.8 d (1H, CHAr, $J = 13.5$ Hz), 3.21 d.t (1H, CHPr, $J = 13.5, 6.5$ Hz), 3.07 d.d (1H, COCH₂, $J = 12.5, 4.5$ Hz), 2.99 t (1H, COCH₂, $J = 12.5$ Hz), 1.4–1.0 m (4H, CH₂CH₂CH₃), 0.8 d (3H, $J = 6.5$ Hz, CH₂CH₂CH₃). Mass spectrum, m/z : M^+ 321. Found, %: C 71.02; H 5.99; N 13.08. $\text{C}_{19}\text{H}_{19}\text{N}_3\text{O}_2$. Calculated, %: C 71.01; H 5.96; N 13.08.

The progress of reactions and the purity of products were monitored by TLC on Silufol UV-254 plates. The IR spectra were recorded on a UR-20 instrument in mineral oil. The ^1H NMR spectra were recorded on a Bruker AM-300 spectrometer at 300 MHz using DMSO- d_6 as solvent. The molecular weights were determined by mass spectrometry using a Finnigan Mat Incos 50 instrument (70 eV).

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