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SHORT COMMUNICATIONS

# Synthesis of 6,6-Dialkyl-4,8-dioxo-5,7-dioxaspiro[2.5]octane-1,1,2,2-tetracarbonitriles and 2,2,3,3-Tetracyanocyclopropanecarboxylic Acid

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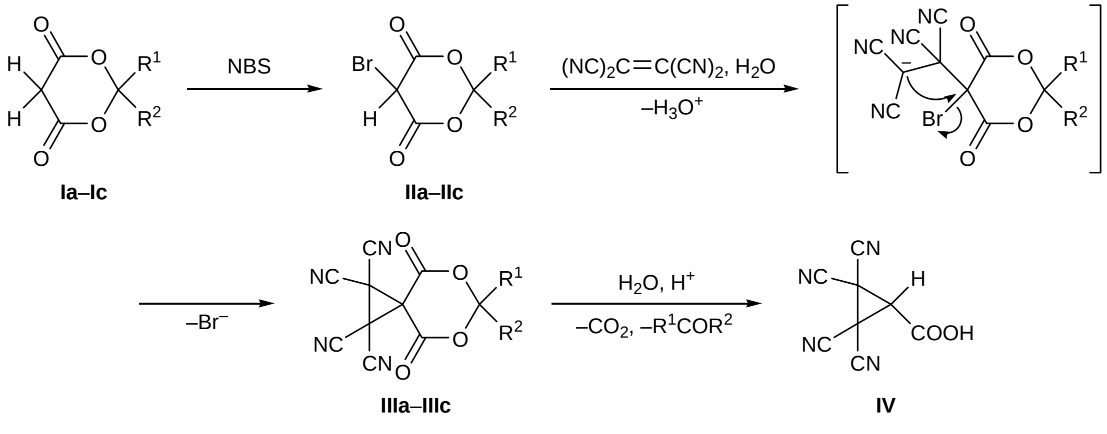
Reaction of tetracyanoethylene with bromo derivatives of compounds possessing an activated methylene group underlies a convenient procedure for the preparation of cyclopropane derivatives with six electron-acceptor groups. This procedure was used previously to synthesize derivatives of aliphatic [1, 2] and aromatic diketones [3], cyanoacetic acid [4], and some heterocyclic compounds having an activated methylene group [5]. However, it was found [6] that diethyl bromomalonate fails to react under analogous conditions, assumingly because of insufficient CH acidity. Therefore, in the present work we used alkylidene malonates **Ia**–**Ic**. The CH acidity of these compounds (which are structurally related to Meldrum’s acid) is comparable with the acidity of acetylacetone [7]. Cyclic esters **Ia**–**Ic** were brominated with *N*-bromosuccinimide in aqueous medium, and the resulting monobromo derivatives **IIa**–**IIc** were brought into reaction with tetracyanoethylene in dioxane. A specific feature of the experimental procedure was the use of finely crushed ice as an “internal” cooling agent and a base. In addition, the presence of water favored crystallization of the products from the reaction mixture. We also found that the product structure depends on the rate of addition of ice. When ice was added quickly, the expected cyclopropane derivatives, 6,6-dimethyl-4,8-dioxo-5,7-dioxaspiro[2.5]octane-1,1,2,2-tetracarbonitriles **IIIa**–**IIIc**, crystallized from the mixture. Upon gradual addition of ice, the product was 2,2,3,3-tetracyanocyclopropanecarboxylic acid (**IV**). Presumably, the latter is formed by hydrolysis of cyclic esters **IIIa**–**IIIc** and subsequent decarboxylation. The structure of compounds **IIIa**–**IIIc** and **IV** was confirmed by the IR, $^1$H NMR, and mass spectra.

**5-Bromo-2,2-dimethyl-1,3-dioxane-4,6-dione (IIa).** Compound **Ia**, 7.2 g (0.05 mol), was dispersed in 30 ml of water under vigorous stirring, and 8.9 g (0.05 mol) of *N*-bromosuccinimide was added in portions at such a rate that the temperature did not exceed 25°C. The mixture was stirred for 15 min and



**Ia**–**Ic** **IIa**–**IIc** **IIIa**–**IIIc** **IV**

$R^1 = R^2 = CH_3$ (**a**), $R^1R^2 = (CH_2)_4$ (**b**), $R^1R^2 = (CH_2)_5$ (**c**).

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filtered, and the colorless precipitate was thoroughly washed with water and dried over $P_2O_5$ under reduced pressure. Yield 80%, mp 80–82°C (decomp.). Bromo derivatives **IIb**, yield 83%, mp 110–113°C (decomp.), and **IIc**, yield 78%, mp 108–110°C (decomp.), were synthesized in a similar way.

**6,6-Dimethyl-4,8-dioxo-5,7-dioxaspiro[2.5]octane-1,1,2,2-tetracarbonitrile (IIIa).** Tetracyanoethylene, 4.48 g (0.035 mol), was dissolved in 100 ml of anhydrous 1,4-dioxane, and 8.9 g (0.04 mol) of compound **IIa** was added to the solution. Finely crushed ice, 200 g, was then added in one portion to the resulting solution under vigorous stirring (the yield and purity of the product depended on the degree of crushing), and the mixture was stirred until the ice thawed completely. The colorless precipitate was filtered off, washed with water and cold 1,4-dioxane, and dried over $P_2O_5$ under reduced pressure. Yield 60%, mp 110–112°C (decomp., from 1,4-dioxane). IR spectrum, ν, $cm^{-1}$: 2280 (C≡N), 1720 (C=O). $^1H$ NMR spectrum (DMSO-$d_6$), δ, ppm: 1.95 s (3H, $CH_3$). Mass spectrum, $m/z$ ($I_{rel}$, %): 270 (5) $[M]^+$, 255 (5), 168 (20), 140 (7), 128 (7), 102 (2), 88 (3), 76 (10), 58 (10), 43 (100).

Compounds **IIIb** and **IIIc** were synthesized in a similar way.

**4,12-Dioxo-5,11-dioxadispiro[2.2.4.2]dodecane-1,1,2,2-tetracarbonitrile (IIIb).** Yield 50%, mp 136–139°C (decomp., from 1,4-dioxane). IR spectrum, ν, $cm^{-1}$: 2280 (C≡N); 1745, 1770 (C=O). $^1H$ NMR spectrum (DMSO-$d_6$), δ, ppm: 2.26 m (4H, $CH_2$), 1.77 m (4H, $CH_2$). Mass spectrum, $m/z$ ($I_{rel}$, %): 296 (0.5) $[M]^+$, 254 (0.5), 168 (10), 140 (5), 128 (14), 115 (15), 88 (18), 84 (100).

**4,13-Dioxo-5,12-dioxadispiro[2.2.5.2]tridecane-1,1,2,2-tetracarbonitrile (IIIc).** Yield 45%, mp 144–145°C (decomp., from 1,4-dioxane). IR spectrum, ν, $cm^{-1}$: 2280 (C≡N); 1750, 1780 (C=O). $^1H$ NMR spectrum (DMSO-$d_6$), δ, ppm: 2.2 m (4H, $CH_2$), 1.75 m (4H, $CH_2$), 1.55 m (2H, $CH_2$). Mass spectrum, $m/z$ ($I_{rel}$, %): 310 (2) $[M]^+$, 282 (2), 168 (2), 140 (4), 128 (12), 98 (80), 88 (20), 55 (100).

**2,2,3,3-Tetracyanocyclopropanecarboxylic acid (IV).** Tetracyanoethylene, 6.4 g (0.05 mol), was dissolved in 100 ml of anhydrous 1,4-dioxane, and 12.3 g (0.055 mol) of compound **IIa** was added to the solution. Ice was added in 0.1–0.5-g portions every 10 min to the resulting solution under vigorous stirring until tetracyanoethylene disappeared from the mixture (test with hydroquinone); 200 g of finely crushed ice was then added, and the mixture was stirred until the ice thawed completely. The mixture was filtered, and the filtrate was left to stand for 2 h. The precipitate was filtered off, washed with water and cold diethyl ether, and dried over $P_2O_5$ under reduced pressure. Yield 35%, mp 134–136°C (decomp., from 1,4-dioxane). IR spectrum, ν, $cm^{-1}$: 3080 (C–H), 2280 (C≡N), 1710 (C=O). $^1H$ NMR spectrum (DMSO-$d_6$), δ, ppm: 4.95 s (1H, CH), 12.15 s (1H, COOH).

The purity of the products was checked by TLC on Silufol UV-254 plates; spots were visualized by irradiation with UV light, treatment with iodine vapor, or heating. The IR spectra were recorded on a UR-20 instrument from samples dispersed in mineral oil. The $^1H$ NMR spectra were obtained on a Bruker DRX-500 spectrometer at a frequency of 500.13 MHz; DMSO-$d_6$ was used as solvent, and TMS, as internal reference. The mass spectra (electron impact, 70 eV) were run on a Finnigan MAT Incos-50 spectrometer.

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