Synthesis of 4,5-dihydroxy-1,3-dinitroimidazolidin-2-one

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A convenient method for the synthesis of 4,5-dihydroxy-1,3-dinitroimidazolidin-2-one from *N,N´*-dinitrourea is developed.

Key words: 4,5-dihydroxy-1,3-dinitroimidazolidin-2-one, *N,N´*-dinitrourea, synthesis.

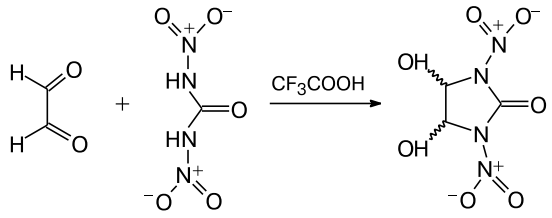
N,N´-Dinitrourea (**1**, DNU) is a high energy compound with high density (1.98 g cm^{-3}) and low thermal stability. It can be used as a precursor of other high energy compounds with the DNU fragment, for example, di- and tetranitroglycolurils. The following information for DNU has been reported: flash point 147—149 °C, decomposition temperature 138—148 °C, spontaneous ignition in air is possible at room temperature;[1] m.p. 107—110 °C (ethyl acetate);[2] fast decomposition at 120 °C (DSC), greater impact and friction sensitivity in comparison with hexogen,[3] temperature of the onset of decomposition is 90 °C, and X-ray data.[4]

The use of the method[2] for the DNU synthesis (nitration of urea with a mixture of nitric and sulfuric acids followed by filtration and washing with dichloromethane), does not allow one to obtain pure DNU (the DNU sample contains up to 20% of sulfuric acid). The attempt to reproduce the other method for the DNU synthesis (nitration of urea with a mixture of nitric and sulfuric acids followed by washing with trifluoroacetic acid)[3] resulted in a yield that was approximately 2.5 times lower (27%) than the yield reported[3] (67%) (a method for DNU synthesis analogous to the method mentioned[3] was also used in the other investigation,[4] the yield was 40%). All the described methods[2—4] are similar to each other in nitration time (1—3 h) and temperature (0—5 °C), but differ in the urea — nitric—sulfuric acid mixture ratio, and also in relative amounts of nitric acid (relative to urea).

We developed a method for the synthesis of DNU that allows one to obtain the product with properties that are well reproducible (some of them are described[5]), and in relatively high yield (64%). Oleum (20%) was used instead of sulfuric acid in the proposed method.

4,5-Dihydroxy-1,3-dinitroimidazolidin-2-one (**2**) is the condensation product of dinitrourea with glyoxal, it has good oxygen balance and lower impact and friction sensitivity in comparison with DNU. This compound has two free positions (hydroxy groups) for further functionalization, therefore, it can be used as a building block for the introduction of 1,3-dinitroimidazolidin-2-one fragment into molecules of organic compounds. The method for its synthesis from DNU and glyoxal described in the literature[6] leads to low yields of the target compound (41.7%). Nitration of 4,5-dihydroxy-2-nitroiminoimidazoline gives compound **2** in 30% yield.[7]

The use of crude DNU (as obtained using the method described earlier[6] and containing up to 20% of sulfuric acid) might be one of the reasons of the low yield of **2** from DNU. We assumed that the use of pure DNU would positively affect the yield of the target product. Initial efforts of the synthesis of compound **2** from pure DNU and aqueous glyoxal were unsuccessful — the hydrolytic decomposition of DNU has occurred (apparently, to nitramide). But when trifluoroacetic acid was used as the reaction medium, the target compound was obtained in 96% yield.



1 **2**

Thus, in the present work we describe the improved method for the synthesis of *N,N´*-dinitrourea and 4,5-dihydroxy-1,3-dinitroimidazolidin-2-one therefrom.

Experimental

^1H and ^{13}C MNR spectra were recorded on a Varian VXR-400 spectrometer using $SiMe_4$ as the internal standard. IR spectra were recorded on a Specord M82 spectrometer, melting points were determined on a Boetius hot stage, the heating rate was 4 deg min^{-1}.

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***N,N′*-Dinitrourea (1).** Urea (7 g, 117 mmol) was added portionwise over 30 min with intensive stirring to sulfuric acid–nitric acid mixture (17 mL of 20% oleum and 17 mL of nitric acid, density ≥1.5 g cm^{-3}) cooled to −15 °C. The reaction mixture was stirred for 1 h at −15 °C and 1.5 h at 0 °C. The precipitate that formed was filtered off, washed with trifluoroacetic acid cooled to 0 °C (5×10 mL), and dried in a vacuum desiccator (waterjet pump vacuum) over calcined K_2SO_4 (or Na_2SO_4) for at least 1.5 h. Yield 11.2 g (64%), m.p. 107—108 °C (decomp.) (lit. data[2]: m.p. 107—111 °C (decomp)). Spectral characteristics of the obtained compound correspond to those described in literature.[2]

4,5-Dihydroxy-1,3-dinitroimidazolidin-2-one (2). An aqueous solution of glyoxal (40%, 6 mL, 41 mmol) was added to a suspension of DNU (5.2 g, 35 mmol) in trifluoroacetic acid (20 mL) with intensive stirring and ice-cooling. The reaction mixture was stirred for 20 h. The crystals that formed were filtered off, washed with trifluoroacetic acid (10 mL), dried on a filter, then in a vacuum desiccator (waterjet pump vacuum) over calcined K_2SO_4 (or Na_2SO_4) for 2 h. Yield 6.9—7.0 g (96—97%), m.p. 162 °C (decomp.), 166—167 °C (decomp., after re-precipitation with dichloromethane from acetone solution); Ref. 6: m.p. 167 °C (decomp.), 175 °C (decomp., after re-precipitation with dichloromethane from acetone solution). Spectral characteristics of the obtained compound correspond to those described in literature.[6]

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