## Development of new methods for the synthesis of 2,3-bis(nitroxymethyl)-2,3-dinitrobutane-1,4-diol dinitrate and its intermediates

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Known methods for the synthesis of 2,3-bis(nitroxymethyl)-2,3-dinitrobutane-1,4-diol dinitrate and its intermediates were investigated. New procedures were developed for the preparation of these compounds. 2,3-Bis(nitroxymethyl)-2,3-dinitrobutane-1,4-diol dinitrate was studied by X-ray diffraction.

**Key words:** 2,3-bis(nitroxymethyl)-2,3-dinitrobutane-1,4-diol dinitrate, 2,3-bis(hydroxymethyl)-2,3-dinitrobutane-1,4-diol, 5,5´-bis(2,2-dimethyl-5-nitro-1,3-dioxane), 2,2-dimethyl-5-hydroxymethyl-5-nitro-1,3-dioxane, phosphorus pentoxide, condensation, dimerization, hydrolysis, nitration, X-ray diffraction.

2,3-Bis(nitroxymethyl)-2,3-dinitrobutane-1,4-diol dinitrate (1) is a new high-energy-density meltable explosive. According to the published data,<sup>1,2</sup> compound 1 has the highest density among all of the known nitrate esters consisting only of carbon, hydrogen, nitrogen, and oxygen atoms. The X-ray density of this compound at 103 K is 1.917 g cm<sup>-3</sup>. This compound has the zero oxygen balance, the enthalpy of formation  $\Delta H^0_{\rm f} = -371$  kJ mol<sup>-1</sup>, and the melting point of 85–86 °C. The sensitivity to friction and the detonation velocity and pressure of this nitrate ester are comparable to octogen, and its sensitivity to impact and the onset of the thermal decomposition are similar to those of pentaerythritol tetranitrate (PETN).<sup>1,2</sup>

Compound 1 was synthesized in 2008 from 2,2-dimethyl-5-hydroxymethyl-5-nitro-1,3-dioxane (2) commercially produced in the United States according to Scheme 1.<sup>2</sup>

The aim of the present work is to experimentally examine the methods for the synthesis of compounds 2-4 and the target compound 1 described in the literature and to develop new procedures for the preparation of these compounds.<sup>3</sup>

As follows from the literature data, compound 2 can be prepared by the condensation of nitroisobutylglycerol (5) with acetone in the presence of *p*-toluenesulfonic acid using the azeotropic distillation of water, which is formed in the course of the reaction, with benzene<sup>4</sup> or by means of the treatment of a suspension of compound 5 in acetone with boron trifluoride etherate<sup>5,6</sup> (Scheme 2).

The investigation of the synthesis methods showed that the former method requires prolonged heating under re-

<sup>†</sup> Deceased.



Scheme 1

*i*. 1) NaOH/H<sub>2</sub>O, 2) Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>; *ii*. MeOH/HCl (gas), 48 h; *iii*. Ac<sub>2</sub>O/AcOH, HNO<sub>3</sub>.

## Scheme 2



**Conditions:** azeotropic distillation of water with benzene in the presence of *p*-toluenesulfonic acid or  $Et_2O \cdot BF_3$ .

flux (for more than 48 h), the yield of the target product being not higher than 27%; the latter method, although producing the target compound 2 in good yield (60–70%),

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requires the use of freshly distilled, difficult-to-obtain, and toxic boron trifluoride etherate, the vapor of which may form an explosive mixture with air.

Compound **2** can be prepared by a procedure developed by us earlier<sup>7</sup> using a more readily available and less toxic phosphorus pentoxide. This method produces the target compound **2** in rather high yield ( $\sim$ 70%).

Compound **3** can be synthesized by methods, which are employed for the dimerization of the sodium salt of 2-nitropropane in the industrial production of 2,3-dimethyl-2,3-dinitrobutane,<sup>8</sup> namely, by the treatment of the sodium salt of compound **2** with bromine, carbon tetrachloride, or sodium persulfate. Under the treatment of the sodium salt of compound **2** with bromine, the yield of compound **3** was 17.2%; with CCl<sub>4</sub>, it was 42.5%; with sodium persulfate, it was 55%.

In order to prepare compound 4, we first repeated the method described earlier<sup>1,2</sup> for the hydrolysis of compound 3 with a methanolic solution of gaseous HCl. This method is not convenient because it requires the use of gaseous HCl and prolonged storage (48 h). Moreover, the distillation of volatile components gave compound 4 as a black resinous substance, which can be successfully crystallized only by the trituration in hot chloroform, the yield of the product being not higher than 27%. The procedure developed by us earlier<sup>9</sup> produced compound 4 in the highest yield. During the treatment of bis(dioxane) 3 with an aqueous-methanol solution of hydrochloric acid under reflux, compound 3 was transformed into solution in 9 h. After the distillation of volatile components, compound 4 was obtained as a pale-amber-colored crystalline substance in almost quantitative yield (97%).

The synthesis of compound 1 by a procedure described earlier<sup>1,2</sup> based on the nitration of compound 4 with a mixture of Ac<sub>2</sub>O, AcOH, and HNO<sub>3</sub> produced tetranitrate 1 in 83% yield, m.p. 84–85 °C (Pr<sup>i</sup>OH). We developed a new, more facile and safe method for the synthesis of compound 1 based on the nitration of compound 3 with nitric acid (Scheme 3).<sup>10</sup>



Scheme 3

This method involves a smaller number of steps, excludes the hydrolysis of compound **3** with corrosion-active HCl that is difficult to implement, and does not require the use of a hazardous explosive mixture of  $Ac_2O$  and  $HNO_3$ , the target compound being produced in rather high yield (68%).

Compound 1 thus synthesized is a white crystalline substance, which is easily soluble in organochlorine solvents (CH<sub>2</sub>Cl<sub>2</sub>, dichloroethane (DCE), *etc.*), acetone, and ethanol and is insoluble in hydrocarbons (hexane and so on). It can be easily purified by the dissolution in dichloromethane followed by the passing of the solution through a column with  $Al_2O_3$  and the addition of *n*-hexane, the fractional distillation of the solvents until the formation of a suspension in *n*-hexane, and the filtration of the precipitate.

The DTA analysis showed (Fig. 1) that compound **1** synthesized by the new method has the melting point of 84.4-86.3 °C, the thermal initial decomposition temperature (IDT) equal to 143 °C, and the temperature of the onset of the extensive thermal degradation equal to 160 °C.

The structure of compound **1** was confirmed by elemental analysis, <sup>1</sup>H, <sup>13</sup>C, and <sup>15</sup>N NMR spectroscopy, IR spectroscopy, mass spectrometry, and X-ray diffraction.

The IR spectrum and the <sup>1</sup>H and <sup>13</sup>C NMR spectra of compound **1** are identical to those reported in the study.<sup>1</sup> Both the electron impact and positive ion (sodium) chemical ionization mass spectra do not show a molecular ion because of its low stability, and only fragment ions at m/z 76(2), 46(100), and 30(31) assigned to the ions [CH<sub>2</sub>ONO<sub>2</sub>]<sup>+</sup>, [NO<sub>2</sub>]<sup>+</sup>, [NO and CH<sub>2</sub>O]<sup>+</sup>, respectively, are observed.

Table 1 gives the crystal lattice parameters of compound **1**, which was purified by the developed procedure, in comparison with the data published in the literature<sup>1</sup> for the crystals obtained by the recrystallization from ethanol. As can be seen from this table, the crystal lattice parameters of compound **1** are equal to those reported previously.<sup>1,2</sup> The difference in the X-ray density of compound **1** is attributed to the fact that the X-ray diffraction experiments were performed at different temperatures (150 and 103 K).

The X-ray density of compound 1 determined at 150 K was  $1.904 \text{ g cm}^{-3}$ . Under the real operating conditions



Fig. 1. TGA and DTA thermal analysis curves for compound 1. M is the relative mass of the sample under study, Q is the normalized heat flow endo down (heat flow referred to the sample mass).

Parameter	Data	
	of this work	published <sup>1</sup>
Molecular formula	$C_{6}H_{8}N_{6}O_{16}$	$C_{6}H_{8}N_{6}O_{16}$
Molecular weight	420.18	420.18
T/K	150	103
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$
Unit cell parameters		
a/Å	8.1377(8)	8.1228(6)
b/Å	23.113(2)	23.0560(16)
c/Å	8.5220(9)	8.5072(6)
α/deg	90.0	90.0
β/deg	113.872(10)	113.950(10)
γ/deg	90.0	90.0
$V/Å^3$	1465.7(3)	1465.01(18)
Ż	4	4
$d_{\rm calc}/{\rm g}~{\rm cm}^{-3}$	1.904	1.917
Absorption coefficient $\mu(M_o)/mm^{-1}$	0.194	0.195

Table 1. Crystallographic parameters for compound 1

(~20 °C), the density of **1** should be lower because the unit cell parameters increase with an increase in the temperature. Actually, we found that the density of compound **1** at 20 °C measured by the flotation method for the crystals, which were obtained from a dichloromethane—hexane mixture, is 1.856 g cm<sup>-3</sup>, for the crystals obtained from isopropyl alcohol, the density is 1.823 g cm<sup>-3</sup> (the difference in the flotation densities is due to the different number of inclusions in the crystals and the sizes of the resulting crystals). Oxley *et al.*,<sup>6</sup> who have repeated the synthesis of compound **1**, obtained a similar result ( $\rho = 1.8238 \text{ g cm}^{-3}$ ).

## Experimental

The <sup>1</sup>H, <sup>13</sup>C, and <sup>15</sup>N NMR spectra were recorded on Bruker AM-300 spectrometers at 300.13, 75.7, and 30.4 MHz, respectively, in CDCl<sub>3</sub> or CD<sub>3</sub>CN. The IR spectra were measured on a Specord M80 spectrometer as KBr pellets. The mass spectra were obtained on a Finnigan MAT INCOS-50 instrument using a direct inlet system at an electron ionization energy of 70 eV. The elemental analysis was carried out on a Perkin-Elmer C,H,N-Analyser instrument. Analytical TLC was performed on Merck TLC Silica gel 60 F<sub>254</sub> plates. The melting points were measured in a capillary. The TGA and DTA thermograms (thermal analysis curves) were obtained on a Diamond TG/DTA Perkin Elmer Thermal Analysis instrument. The heating rate was 5 °C min<sup>-1</sup> in the range of 20–240 °C. The X-ray diffraction study of the reaction product was performed on a SMART APEX 2 CCD diffractometer (graphite monochromator,  $\lambda$ (Mo-K $\alpha$ ) radiation,  $\varphi$ - and  $\omega$ -scanning technique,  $\theta_{max} = 27^{\circ}$ , 150 K).

Nitroisobutylglycerol was prepared by a known procedure.<sup>11</sup> The other compounds used in this study are commercially available.

**2,2-Dimethyl-5-hydroxymethyl-5-nitro-1,3-dioxane (2).** Phosphorus pentoxide (5 g, 0.035 mol) was added in one portion with

stirring at 10 °C to a mixture of compound 5 (15.1 g, 0.1 mol) and acetone (50 mL, 0.68 mol). The reaction mixture was stirred for 10 min and poured into a mixture (100 mL) of a saturated potassium carbonate solution and ice. Then the reaction mixture was stirred until the ice disappeared. The precipitate that formed was filtered off, washed with cold water, and dried in air. Compound 2 was obtained in a yield of 13.5 g (71%), m.p. 132-134 °C (acetone) (cf. lit. data<sup>5</sup>: m.p. 133–134 °C). According to the TLC data and the IR spectrum, this compound is identical to the product prepared by a method described earlier.<sup>5</sup>  $R_f = 0.67$  (ethyl acetate—hexane, 1 : 1, as the eluent). IR (KBr),  $\nu/cm^{-1}$ : 3427, 3002, 2949, 2893, 1542, 1443, 1386, 1352, 1319, 1266, 1251, 1206, 1149, 1091, 1061, 1027, 825, 732, 568, 518. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>), δ: 1.42 (s, 3 H, C<u>H</u><sub>3</sub>); 1.44 (s, 3 H, C<u>H</u><sub>3</sub>); 2.08-2.19 (br.s, 1 H, OH); 3.99-4.43 (m, 4 H, CH<sub>2</sub>O); 4.06 (s, 2 H, CH<sub>2</sub>OH).

5,5'-Bis(2,2-dimethyl-5-nitro-1,3-dioxane) (3). A. Compound 2 (3.22 g, 0.02 mol) was added with stirring to a solution of NaOH (0.96 g, 0.024 mol) in water (32 mL). The suspension was heated to 60 °C and stirred for 40 min. The wine-colored solution was cooled to 20 °C, bromine (1.76 g, 0.011 mol) was dosed at this temperature, and the reaction mixture was stirred for 30 min. Then ethanol (4 mL) was added, and the mixture was refluxed for 10 h, the pH value of the reaction mixture being maintained equal to 12 by adding an aqueous NaOH solution. After the completion of the reaction, the mixture was cooled to 10 °C and diluted with water (10 mL). The precipitate was filtered off and successively washed with a 5% NaOH solution  $(2 \times 10 \text{ mL})$  and water  $(2 \times 15 \text{ mL})$ . Compound 3 was obtained in a yield of 0.55 g (17.2%), m.p. 128–129 °C (cf. lit. data<sup>1,2</sup>: m.p. 129-130 °C). During TLC, the product gives one spot with  $R_{\rm f} = 0.88$  (ethyl acetate—hexane, 1 : 1, as the eluent). IR (KBr), v/cm<sup>-1</sup>: 3002, 2945, 2886, 1570, 1382, 1338, 1202, 1123, 1081, 952, 828, 581, 527. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>), δ: 1.35 (s, 6 H, CH<sub>3</sub>); 1.41 (s, 6 H, CH<sub>3</sub>); 4.29–4.49 (m, 8 H, CH<sub>2</sub>O). According to the TLC data, the IR spectrum, and the <sup>1</sup>H NMR spectrum, this compound is identical to that prepared by a method described earlier.12

**B.** Dimethyl sulfoxide (10 mL) was placed in a flask equipped with a stirrer, a thermometer and a reflux condenser, and then compound **2** (3.22 g, 0.02 mol) was added with stirring. At 20–25 °C, a solution of NaOH (0.8 g, 0.02 mol) in water (1.2 mL) was dosed. The wine-colored solution was stirred at 25–30 °C for 40 min, and CCl<sub>4</sub> (2.4 mL, 3.85 g, 0.025 mol) was added. Then the reaction mixture was warmed to 55 °C and stirred at this temperature for 8 h. The content of the flask was cooled to 15 °C and diluted with water (30 mL). The yellow precipitate that formed was filtered off and successively washed with a 10% NaOH solution (3×15 mL) and water (3×15 mL) until a neutral reaction of the wash water. Compound **3** was obtained in a yield of 1.36 g (42.5%), m.p. 129–131 °C (ethanol). According to the TLC data, the IR spectrum, and the <sup>1</sup>H NMR spectrum, this compound is identical to that prepared by the method **A**.

**C.** Compound **2** (64 g, 0.33 mol) was added with stirring at 20 °C to a solution of NaOH (26.8 g, 0.67 mol) in water (0.5 L). The reaction mixture was warmed to 60 °C for 1 h and then cooled to 20 °C. Solid sodium persulfate (159.5 g, 0.67 mol) was added in one portion. The resulting mixture was stirred at 20 °C for 4 h and allowed to stand at room temperature for two days, during which a white precipitate of compound **3** formed. Then pH of the reaction mixture was adjusted to >11 by adding

a concentrated NaOH solution. The precipitate was filtered off, washed with cold water, and dried in air. Compound **3** was obtained in a yield of 30 g (55%), m.p. 129–131 °C (ethanol). According to the TLC data, the IR spectrum, and the <sup>1</sup>H NMR spectrum, this compound is identical to that prepared by the method **A**.

**2,3-Bis(hydroxymethyl)-2,3-dinitrobutane-1,4-diol (4).** Water (16 mL), methanol (4 mL), concentrated hydrochloric acid (1 mL), and compound **3** (3.5 g, 0.011 mol) were placed in a stirred vessel equipped with a reflux condenser. The resulting suspension was heated with stirring to reflux and maintained until compound **3** completely dissolved (~9 h). Then volatile products were removed from the reaction mixture in a water-jet pump vacuum. Compound **4** was obtained in a yield of 2.55 g (97%) as pale-amber-colored crystals, m.p. 102 °C (*cf.* lit. data<sup>1,2</sup>: m.p. 100–102 °C),  $R_f = 0.71$  (acetone—methanol, 1 : 1, as the eluent). MS [M + Na]<sup>+</sup>: Found (%): 263.0477, 264.0507, 265.0519.  $C_6H_{12}N_2O_6$ . Calculated (%): 263.0486, 264.0519. <sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>CN),  $\delta$ : 2.95–3.11 (br.s, 4 H, O<u>H</u>); 4.17–4.29 (m, 8 H, C<u>H</u><sub>2</sub>).

2,3-Bis(nitroxymethyl)-2,3-dinitrobutane-1,4-diol dinitrate (1). 98% Nitric acid (210 mL) was placed in a stirred vessel and cooled to a temperature from -2 to -10 °C. Then urea (6 g) was added with stirring. After the complete dissolution of the urea, compound 3 (15.0 g, 0.047 mol) was added portionwise with stirring at this temperature for 15 min. The reaction mixture was stirred at a temperature from 0 to -5 °C for 3 h and then poured with vigorous stirring into ice water (1000 mL). The pale-gray precipitate that formed was filtered off, washed with ice water, dried, and recrystallized from isopropyl alcohol. The target product was obtained in a yield of 13.4 g (68%), m.p. 82 °C. After the purification by the above-described procedure, target compound 1 was obtained in a yield of 11.1 g (56.4%), m.p. 84-86 °C (cf. lit. data<sup>1,2</sup>: m.p. 85–86 °C). Found (%): C, 17.37; H, 1.65; N, 19.80. C<sub>6</sub>H<sub>8</sub>N<sub>6</sub>O<sub>16</sub>. Calculated (%): C, 17.15; H, 1.92; N, 20.0. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>),  $\delta$ : 5.03–5.35 (m, 8 H, C<u>H</u><sub>2</sub>). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>), δ: 66.1 (4 C, <u>CH<sub>2</sub></u>); 89.1 (2 C, <u>CH<sub>2</sub></u>). <sup>15</sup>N NMR (30 MHz, CD<sub>3</sub>CN), δ: -50.6 (s, 4 N, ONO<sub>2</sub>); -9.2 (s, 2 N, NO<sub>2</sub>). IR (KBr), v/cm<sup>-1</sup>: 3436, 3046, 3028, 2990, 2982, 2927, 1694, 1674, 1658, 1583, 1573, 1491, 1466, 1451, 1390,

1371, 1335, 1287, 1274, 1157, 1100, 1057, 1023, 995, 899, 869, 854, 831, 714. MS, m/z ( $I_{rel}$  (%)): 76 (2) [CH<sub>2</sub>ONO<sub>2</sub>]<sup>+</sup>, 46 (100) [NO<sub>2</sub>]<sup>+</sup>, 30 (31) [NO and CH<sub>2</sub>O]<sup>+</sup>.

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