

# Synthesis of 1,1-bis(methoxy-*NNO*-azoxy)-3,3,3-trinitropropane from 1,1-bis(methoxy-*NNO*-azoxy)ethene and nitroform

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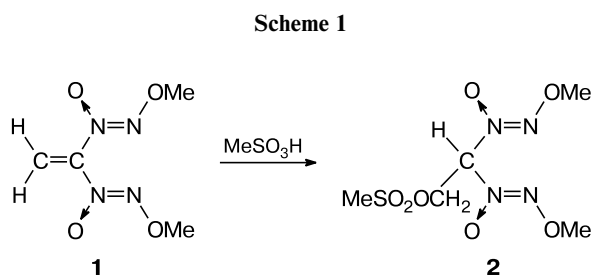
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A reaction of 1,1-bis(methoxy-*NNO*-azoxy)ethene with nitroform at  $\sim 20^\circ\text{C}$  gave 1,1-bis(methoxy-*NNO*-azoxy)-3,3,3-trinitropropane.

**Key words:** alkoxy-*NNO*-azoxy compounds, 1,1-bis(methoxy-*NNO*-azoxy)-3,3,3-trinitropropane, 1,1-bis(methoxy-*NNO*-azoxy)ethene, nitroform, the Michael reaction, NMR spectroscopy.

In the last 30 years, alkoxydiazene *N*-oxides (ADO)  $\text{R}-\text{N}(\text{O})=\text{N}-\text{O}-\text{R}'$  have attracted the attention of researchers as promising components for energetic materials.<sup>1,2</sup> Having the same elemental composition as secondary nitramines  $\text{R}-\text{N}(\text{NO}_2)-\text{R}'$ , which have long been used widely as explosives and propellant components, ADO are superior to them in the enthalpy of formation (by 6–15 kcal mol<sup>-1</sup> per group  $\text{N}_2\text{O}_2$ ).<sup>3</sup> Usually, ADO have lower densities and higher melting points than secondary nitramines and are thermally stable and chemically inert. In the last few years, ADO have been considered to be components of gas-generating compositions for automobile airbags.<sup>4</sup>

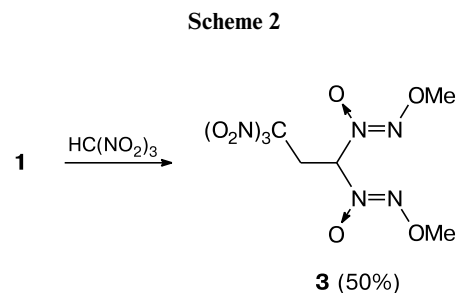
Recently,<sup>5</sup> we have obtained earlier unknown 1,1-bis(methoxy-*NNO*-azoxy)ethene (**1**) and found that this compound can add weakly nucleophilic methanesulfonic acid to give 2,2-bis(methoxy-*NNO*-azoxy)ethyl methanesulfonate (**2**) (Scheme 1).



We hoped that olefin **1** could be employed in the Michael condensation with high-energy acids (in particular, nitroform). Like other polynitroalkanes, nitroform can act as a good Michael donor toward various activated olefins.<sup>6</sup> A detailed study of the addition of nitroform to methyl acrylate revealed that the rate-limiting step of this addition in acidic and neutral media is a nucleophilic at-

tack of the nitroform carbanion on the C(3) atom of methyl acrylate.<sup>6</sup> In electronic structure, olefin **1** is most similar to mononitroalkenes.<sup>5</sup> Nitroalkenes readily add nitroform, also in the absence of a catalyst.<sup>6–11</sup>

Indeed, compound **1** reacts with nitroform at  $\sim 20^\circ\text{C}$  for several hours to give 1,1-bis(methoxy-*NNO*-azoxy)-3,3,3-trinitropropane (**3**) (Scheme 2).



The low yield of compound **3** is probably due to the losses upon isolation and purification, because the reaction mixture contains only the target product **3** and the excess nitroform (TLC). Compound **3** crystallizes from diethyl ether as a solvate (m.p. 40–43  $^\circ\text{C}$ ) with  $\text{Et}_2\text{O}$  ( $\sim 1.4$  mol, calculated from the mass balance), which is slowly released in air drying at  $\sim 20^\circ\text{C}$ .

Colorless crystals of compound **3** (m.p. 107.5–108.7  $^\circ\text{C}$ , from  $\text{CH}_2\text{Cl}_2-\text{Bu}^t\text{OMe}$  (1 : 10)) are sensitive to mechanical impact (they crackle when ground in a porcelain mortar but are insensitive to grinding in an agate mortar).

Structure **3** was proved by elemental analysis and  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{14}\text{N}$  NMR spectroscopy. In the  $^1\text{H}$  NMR spectrum of compound **3** in  $\text{CDCl}_3$ , the singlet for the methoxy group ( $\delta$  4.10) has nearly the same chemical shift as an analogous signal for ester **2** ( $\delta$  4.12)<sup>5</sup> and is slightly shifted downfield compared to the signal for olefin **1**

( $\delta$  4.19).<sup>5</sup> The triplet for the  $\text{CH}(\text{N}_2\text{O}_2\text{Me})_2$  proton ( $\delta$  6.39) is shifted downfield compared to an analogous signal in the spectrum of compound **2** ( $\delta$  6.21).<sup>5</sup> The  $^{13}\text{C}$  NMR spectrum of compound **3** shows a signal for the MeO group at  $\delta$  62.86, which falls within the range characteristic of some other geminal methoxy-*NNO*-azoxy compounds ( $\delta$  60–63 in  $\text{CDCl}_3$ ).<sup>5,12</sup> The signal for the trinitromethyl group is masked with noise signals because of its large broadening due to the quadrupole effect of the  $^{14}\text{N}$  nuclei and its lower integral intensity due to the weaker NOE and the longer spin-lattice relaxation time under standard conditions of the  $^{13}\text{C}$  NMR experiment. The  $^{14}\text{N}$  NMR spectrum contains two signals. The relatively narrow signal is due to three geminal nitro groups ( $\delta$  –32.6,  $\Delta\nu_{1/2} = 20$  Hz). The signal for the *N*-oxide nitrogen atom of the group  $\text{N}(\text{O})=\text{NOMe}$  is shifted upfield and is wider than the signal for the nitro groups ( $\delta$  –77,  $\Delta\nu_{1/2} = 330$  Hz). The corresponding signals in the  $^{14}\text{N}$  NMR spectra of compounds **1** and **2** (see Ref. 5) and (methoxy-*NNO*-azoxy)ethene<sup>13</sup> appear at  $\delta$  –80 ( $\Delta\nu_{1/2} = 205$  Hz), –78 (300), and –67 (80). The integral intensity ratio of the signals in the  $^{14}\text{N}$  NMR spectrum of compound **3** (~3 : 2) is proportional to the number of the corresponding N atoms in its molecule.

To sum up, the reaction of 1,1-bis(methoxy-*NNO*-azoxy)ethene with nitroform at ~20 °C afforded earlier unknown 1,1-bis(methoxy-*NNO*-azoxy)-3,3,3-trinitropropane (**3**) combining dissimilar high-energy groups: trinitromethyl and two geminal methoxy-*NNO*-azoxy ones.

### Experimental

NMR spectra (300 ( $^1\text{H}$ ), 75 ( $^{13}\text{C}$ ), and 36.14 MHz ( $^{14}\text{N}$ )) were recorded on a Bruker Avance 300 SF spectrometer in  $\text{CDCl}_3$  with  $\text{SiMe}_4$  as the internal standard ( $^1\text{H}$ ,  $^{13}\text{C}$ ) and with  $\text{MeNO}_2$  as the external standard ( $^{14}\text{N}$ ). Signals for the protons were assigned as described earlier.<sup>5,12–14</sup> Elemental analysis was carried out on a Vario MICRO cube CHNS analyzer. 1,1-Bis(methoxy-*NNO*-azoxy)ethene (**1**) was prepared as described earlier.<sup>5</sup>

**1,1-Bis(methoxy-*NNO*-azoxy)-3,3,3-trinitropropane (3).** A mixture of compound **1** (286 mg, 1.63 mmol) and nitroform (460 mg, 3 mmol) was stirred at 30–40 °C to homogenization (10 min) and left at ~20 °C for three days (TLC, Silufol,  $\text{AcOEt}-\text{C}_6\text{H}_6$  (1 : 3);  $R_f$  0.28 (**1**), 0.55 (**3**), 0–0.8 (nitroform as a yellow trace slightly visualized under UV light)). After 3 h, the reaction mixture contained only the traces of compound **1**. The mixture was dissolved in  $\text{CH}_2\text{Cl}_2$  (2 mL) and passed through silica gel (Sapelko, 40–60  $\mu\text{m}$ , 2 g). The silica gel was washed with  $\text{CH}_2\text{Cl}_2$  (10 mL) and the combined filtrate was concentrated *in vacuo*. The residue (0.48 g) was recrystallized from  $\text{Et}_2\text{O}$  (1 mL) at –18 °C, washed with cold (–30 °C)  $\text{Et}_2\text{O}$  (5 mL), and dried under argon for 0.5 h. The resulting colorless crystals (325 mg, m.p. 40–43 °C) almost completely lost the solvated  $\text{Et}_2\text{O}$  on keeping in air for two days. The content of  $\text{Et}_2\text{O}$  in the final product was 8 mol.% ( $^1\text{H}$  NMR). The yield of compound **3** was 270 mg (50%), m.p. 107.1–107.6 °C. Upon recrystallization from  $\text{CH}_2\text{Cl}_2-\text{Bu}^t\text{OMe}$  (~1 : 10 v/v), m.p. 107.5–108.7 °C (heating rate 1.5 deg  $\text{min}^{-1}$ ); the melt decomposed slowly above the melting point. Found (%): C, 18.40; H, 2.80; N, 29.49.

$\text{C}_5\text{H}_9\text{N}_7\text{O}_{10}$ . Calculated (%): C, 18.36; H, 2.77; N, 29.97.  $^1\text{H}$  NMR,  $\delta$ : 4.10 (s, 6 H, OMe); 4.33 (d, 2 H,  $\text{CH}_2$ ,  $J = 6.0$  Hz); 6.39 (t, 1 H, CH,  $J = 6.0$  Hz).  $^{13}\text{C}$  NMR,  $\delta$ : 32.1 ( $\text{CH}_2$ ); 62.9 ( $\text{CH}_3\text{O}$ ); 86.5 ( $\text{CHN}_2$ ).  $^{14}\text{N}$  NMR,  $\delta$ : –77 (2 N,  $\text{N}(\text{O})=\text{N}$ ,  $\Delta\nu_{1/2} \approx 330$  Hz); –32.6 (3 N,  $\text{NO}_2$ ,  $\Delta\nu_{1/2} \approx 20$  Hz).

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