

Synthesis of Mixed Plasticizers Containing *N,N'*-Bis(nitrooxyalkyl)-*N,N'*-dinitromethanediamines

V. A. Tartakovskii, A. S. Ermakov, N. V. Sigai, and S. A. Serkov

Zelinskii Institute of Organic Chemistry, Russian Academy of Sciences, Leninskii pr. 47, Moscow, 117913 Russia
e-mail: ermakov@ioc.ac.ru

Received February 10, 2005

Abstract—New mixed plasticizers for gas-generating compositions on the basis of nitrooxy derivatives of *N,N'*-dialkyl-*N,N'*-dinitromethanediamines were obtained by condensation of *N*-hydroxyalkylsulfamates with formaldehyde, followed by nitration.

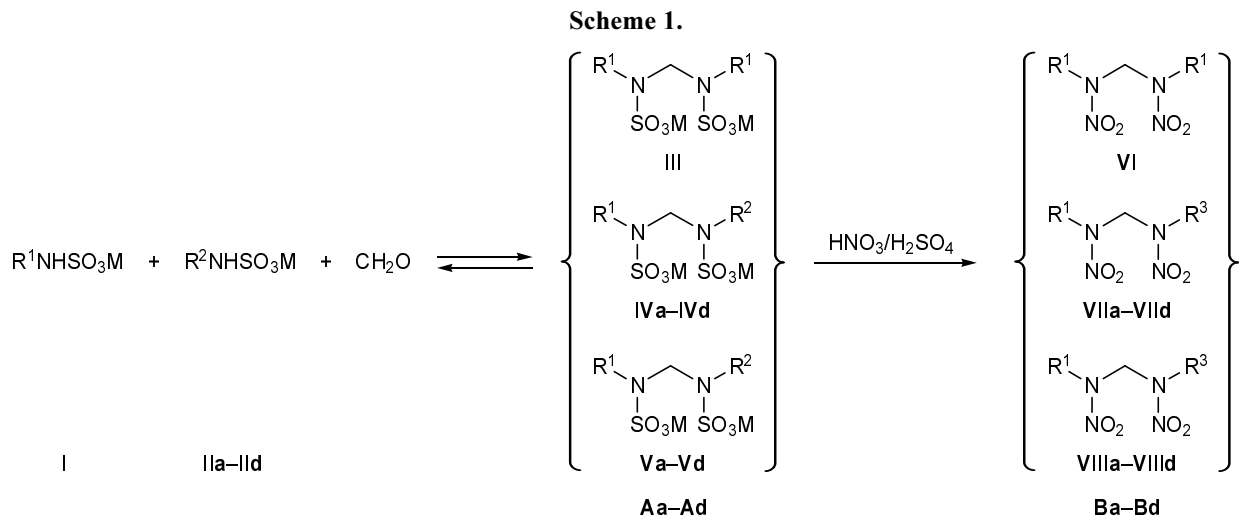
DOI: 10.1134/S1070428006070025

N,N'-Dialkyl-*N,N'*-dinitromethanediamines have recently been proposed as components of high-energy compositions [1]. We continued studies in this line and synthesized a new plasticizer for gas-generating compositions, which was a mixture of 2,4-dinitro-2,4-diazapentane, 2,4-dinitro-2,4-diazahexane, and 3,5-dinitro-3,5-diazahexane (so-called ternary mixture “TS CH₃/C₂H₅”) [2].

However, the obtained plasticizer was characterized by a low concentration of oxygen, and it did not meet all requirements imposed on components of gas-generating compositions. Therefore, synthesis of new energy-rich components and development of more

convenient methods for their preparation remain important problems. We believed that the synthesis of *N,N'*-dialkyl-*N,N'*-dinitromethanediamines having nitrooxy groups will help us to solve the above problems. We previously showed that the condensation of two different *N*-alkylsulfamates with formaldehyde, followed by nitration, gives a mixture of *N,N'*-dialkyl-*N,N'*-dinitromethanediamines [3]. In the present work we tried to extend the scope of this reaction to *N*-hydroxyalkylsulfamates **IIa–IIId** (Scheme 1).

Since the condensation of *N*-alkylsulfamates with formaldehyde is a reversible process, it is necessary to remove water liberated during the reaction to displace



I, III, VI, R¹ = CH₃; **II**, R² = HO(CH₂)₂ (**a**), HO(CH₂)₃ (**b**), HO(CH₂)₄ (**c**), CH₃CH(OH)CH₂ (**d**); **IV**, R¹ = CH₃, R² = HO(CH₂)₂ (**a**), HO(CH₂)₃ (**b**), HO(CH₂)₄ (**c**), CH₃CH(OH)CH₂ (**d**); **V**, R¹ = R² = HO(CH₂)₂ (**a**), HO(CH₂)₃ (**b**), HO(CH₂)₄ (**c**), CH₃CH(OH)CH₂ (**d**); **VII**, R¹ = CH₃, R³ = O₂NO(CH₂)₂ (**a**), O₂NO(CH₂)₃ (**b**), O₂NO(CH₂)₄ (**c**), CH₃CH(ONO₂)CH₂ (**d**); **VIII**, R¹ = R³ = O₂NO(CH₂)₂ (**a**), O₂NO(CH₂)₃ (**b**), O₂NO(CH₂)₄ (**c**), CH₃CH(ONO₂)CH₂ (**d**); M = Na, K, NH₄.

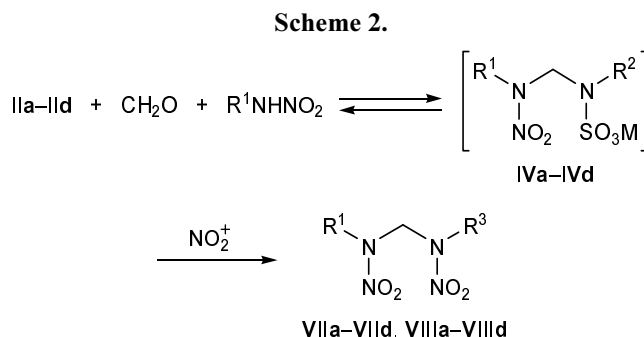
the equilibrium toward the condensation products. This may be achieved in two ways. The first of these implies that the condensation is carried out with sodium, potassium, or ammonium *N*-methylsulfamate (**I**) and the corresponding *N*-hydroxyalkylsulfamic acid salt **IIa–IIId** in aqueous formaldehyde, followed by vacuum distillation of water at 70–90°C; as a result, mixtures of condensation products (**Aa–Ad**) are obtained. According to the second method, the liberated water is bound by sulfuric acid.

The condensation performed according to the first method gave compounds whose IR spectra contained absorption bands typical of NSO₃K (1180–1230 cm⁻¹) and OH groups (3400–3600 cm⁻¹). The condensation products were then subjected to nitration with a mixture of concentrated nitric and sulfuric acids. We found that the yield and product ratio depend on the initial reactant ratio, pH in the condensation stage, and nitration conditions. The maximal yields of ternary mixtures **Ba–Bd** reached 50–75% at pH 5–6 when the subsequent nitration was performed in 92–94% H₂SO₄ at –20°C over a period of 60–70 min. Under these conditions, the composition of the resulting ternary mixtures approached the theoretical value determined by the ratio of the initial *N*-methyl- and *N*-hydroxyalkylsulfamates.

Increase of the nitration time or rise in temperature changed the composition or resulted in reduced yield of the ternary mixture. For example, the maximal yield of mixture **Ba** was 64% (nitration temperature –20°C, 2 h), but its composition differed from that calculated for equimolar ratio of the initial sulfamates, mol %: **VI**:**VIIa**:**VIIIa** = 37:55:8 against 25:50:25. When the nitration was carried out at 0°C, the yield of **Ba** decreased to 44%, but its composition only slightly differed from the theoretical ratio, mol %: **VI**:**VIIa**:**VIIIa** = 26:52:22. The composition of ternary mixtures was determined by ¹H NMR spectroscopy from the intensity ratio of the signals from the methylene protons between the nitroamino groups and methyl protons in 2,4-dinitro-2,4-diazapentane (**VI**) and unsymmetrical component.

In order to identify components of the obtained mixtures and determine their physicochemical properties we synthesized individual *N*-methyl-*N'*-nitrooxyalkyl- and symmetric *N,N'*-bis(nitrooxyalkyl)-*N,N'*-dinitromethanediamines by condensation of *N*-hydroxyalkylsulfamates **IIa–IIId** with *N*-methyl- or the corresponding *N*-nitro- ω -nitrooxyalkylamines and formal-

dehyde and subsequent nitration of the condensation products with 97% HNO₃ or a mixture of nitric acid with acetic anhydride [3] (Scheme 2).



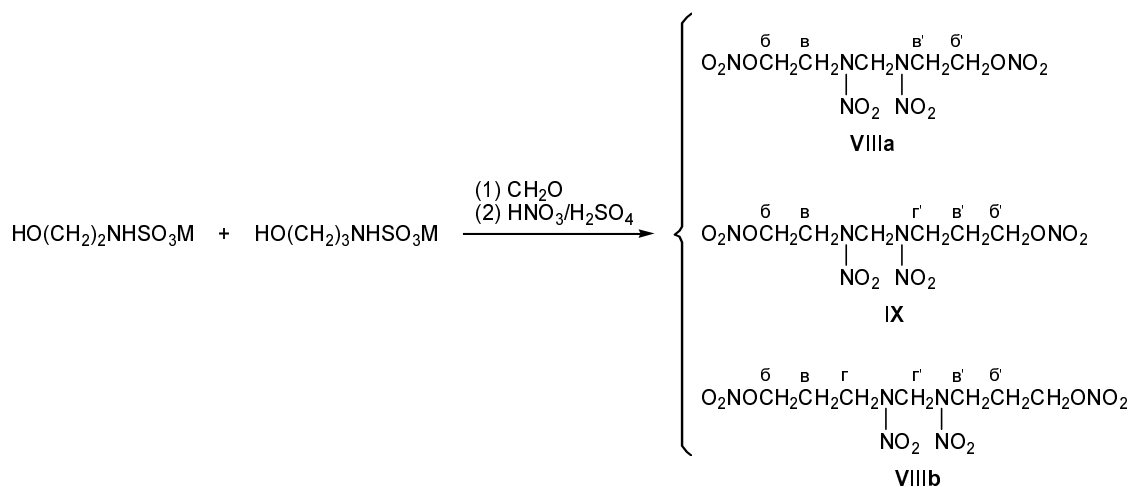
Following the procedure for the synthesis of mixtures **Ba–Bd**, we obtained ternary mixture **C** consisting of 3,5-dinitro-1,7-dinitrooxy-3,5-diazaheptane (**VIIIa**), 3,5-dinitro-1,8-dinitrooxy-3,5-diazaoctane (**IX**), and 4,6-dinitro-1,9-dinitrooxy-4,6-diazanonane (**VIIIb**) (Scheme 3). The condensation of potassium (sodium or ammonium) salts of *N*-(hydroxyethyl)- and *N*-(hydroxypropyl)sulfamic acids with 33% aqueous formaldehyde was carried out at pH 5–6. After removal of water by distillation we isolated the condensation product as a nonhygroscopic powder with mp 140°C. The subsequent nitration with a mixture of concentrated nitric acid and 97% H₂SO₄ at –10 to –15°C (nitration time 60 min) gave mixture **C** in 56% yield.

For identification of the components of mixture **C** we synthesized compounds **VIIIa** and **VIIIb** with a purity of 99%; however, we failed to obtain unsymmetrically substituted compound **IX** with an acceptable purity. By analogy with our experimental data on ternary mixtures **Ba–Bd**, we presumed that the “mixed” product in mixture **C** has structure **IX**. In addition, this structure follows with a high probability from the spectral parameters of individual compounds **VIIIa** and **VIIIb** and ternary mixture **C**:

First, protons in the ethylene fragment of compound **IX** resonate in the ¹H NMR spectrum of mixture **C** in the region corresponding to analogous protons of compound **VIIIa**, at δ 4.01–4.11 and 3.63–3.77 ppm, and protons in the trimethylene fragment of **IX** give signals in the same regions as those of compound **VIIIb**, at δ 3.83–3.91, 3.49–3.70, and 1.61 ppm;

Second, the proton–proton coupling constant $J_{\alpha,\beta}$ in the spectrum of **VIIIa** is equal to the coupling constant for the ethylene protons in **IX**: $J_{\alpha,\beta}(\text{VIIIa}) = J_{\alpha,\beta}(\text{IX}) =$

Scheme 3.



5.3 Hz, while the coupling constants for protons in the γ' -, β' -, and α' -positions of compound **VIIIb** are equal to the corresponding coupling constants for the trimethylene fragment in **IX**: $J_{\gamma',\beta'}(\text{VIIIb}) = J_{\gamma',\beta'}(\text{IX}) = 7.1$ Hz and $J_{\alpha',\beta'}(\text{VIIIb}) = J_{\alpha',\beta'}(\text{IX}) = 6.0$ Hz;

Third, the signal intensity ratios for the CH_2 protons in **IX**, $\text{C}^{\gamma'}\text{H}_2/\text{C}^{\beta'}\text{H}_2$ and $\text{C}^{\alpha'}\text{H}_2/\text{C}^{\alpha}\text{H}_2$ are equal to unity, indicating the integrity of molecule **IX**.

The signals of compounds **VIIIa** and **VIIIb** in the ^1H NMR spectrum of mixture **C** are slightly displaced downfield.

The use of sulfuric acid as both component of the nitrating mixture and dehydrating agent in the condensation of *N*-alkylsulfamates with formaldehyde makes the preparation of ternary mixtures **Ba–Bd** simpler (second method). According to this method, initial *N*-alkylsulfamates and paraformaldehyde were taken at a molar ratio of 1:1:1.1 and were added to sulfuric acid at 10–20°C, the mixture was stirred for 0.5 h and added to nitric acid cooled to –15 to –20°C, and the resulting mixture was stirred for 1 h at that temperature.

The main factor determining the yield and composition of mixed plasticizers was the concentration of sulfuric acid. Change of the sulfuric acid concentration from 85 to 94% increases the yield of mixtures **Ba–Bd** from 35 to 60%. However, the mixtures thus obtained were enriched in compound **VI**, as compared to its theoretical fraction (25%); the reason is the low stability of *N*-hydroxyalkylsulfamates in acid media: they should reside in acid no longer than it is necessary for their dissolution.

Thus we have synthesized new mixed plasticizers containing alkyl nitrate moieties. Preliminary tests showed that the new compositions exhibit a good plasticizing ability toward nitrocellulose containing 12.4 to 13.2% of nitrogen (the compositions were tested at the Mendeleev Russian University of Chemical Technology, Moscow).

EXPERIMENTAL

The IR spectra were recorded in KBr on a Specord M-60 instrument. The ^1H NMR spectra were measured on a Bruker WM-250 spectrometer at 250.13 MHz using benzene- d_6 as solvent and HMDS as internal reference.

Nitrooxydinitrodiazaalkanes VIIa–VIIId (general procedure). Potassium, sodium, or ammonium *N*-hydroxyalkylsulfamate, 10 mmol, 0.91 g (12 mmol) of *N*-nitromethanamine, and 0.95 g of 30% aqueous formaldehyde were added to 10 ml of 40% aqueous ethanol. The mixture was adjusted to pH ~5.5 and evaporated to dryness under reduced pressure. The residue was washed with diethyl ether, dried, and added to 98% HNO_3 cooled to –20 to –25°C (10 ml of nitric acid was taken for 3 g of the condensation product). The mixture was stirred for 1 h at –20°C, poured into 20 ml of an ice–water mixture, and extracted with chloroform (2 × 10 ml). The extract was washed with water (2 × 10 ml), a 3% solution of Na_2CO_3 (2 × 10 ml), and water again (10 ml) and evaporated to dryness.

3,5-Dinitro-3,5-diazahexyl nitrate (VIIa). Yield 68%, mp 54°C [3]. ^1H NMR spectrum, δ , ppm: 3.50 s

(3H, CH₃N), 3.70 t (2H, NCH₂C, $J = 5.3$ Hz), 4.05 t (2H, CH₂ONO₂, $J = 5.3$ Hz), 4.81 s (2H, NCH₂N).

4,6-Dinitro-4,6-diazaheptyl nitrate (VIIb). Yield 75%, mp 38°C. ¹H NMR spectrum, δ , ppm: 1.60 m (2H, CCH₂C), 3.48 s (3H, CH₃N), 3.51 t (2H, NCH₂C, $J = 7.1$ Hz), 3.83 t (2H, CH₂ONO₂, $J = 6.0$ Hz), 4.81 s (2H, NCH₂N). Found, %: C 23.75; H 4.32. C₅H₁₁N₅O₇. Calculated, %: C 23.72; H 4.35.

5,7-Dinitro-5,7-diazaoctyl nitrate (VIIc). Yield 45%, yellow oily substance. ¹H NMR spectrum, δ , ppm: 1.8–1.9 m (4H, CCH₂CH₂C), 3.50 s (3H, CH₃N), 3.85 t (2H, NCH₂C, $J = 6.5$ Hz), 4.20 t (2H, CH₂ONO₂, $J = 7.3$ Hz), 4.90 s (2H, NCH₂N). Found, %: C 23.75; H 4.32. C₆H₁₃N₅O₇. Calculated, %: C 26.98; H 4.90.

1-Methyl-3,5-dinitro-3,5-diazaheptyl nitrate (VIIId). Yield 55%, mp 68°C. ¹H NMR spectrum, δ , ppm: 1.49 d.d (3H, CCH₃, $J = 2.5, -5.9$ Hz), 3.51 s (3H, CH₃N), 4.15 m (2H, NCH₂C), 4.75 m (1H, CHONO₂), 4.86 s (2H, NCH₂N). Found, %: C 23.51; H 4.30; N 27.22. C₅H₁₁N₅O₇. Calculated, %: C 23.72; H 4.35; N 27.67.

Dinitrooxydinitrodiazaalkanes VIIa–VIIId were synthesized by the procedure described above for compounds VIIa–VIIId from the corresponding *N*-hydroxyalkylsulfamic acid salt (instead of *N*-nitromethanamine), 30% aqueous formaldehyde, and *N*-nitroaminoalkyl nitrate; the condensation was carried out at pH 6.5.

3,5-Dinitro-3,5-diazaheptane-1,7-diyl dinitrate (VIIIa). Yield 65%, mp 92–93°C [3]. ¹H NMR spectrum, δ , ppm: 3.63 t (2H, NCH₂C, $J = 5.3$ Hz), 4.04 t (2H, CH₂ONO₂, $J = 5.3$ Hz), 4.84 t (1H, NCH₂N).

4,6-Dinitro-4,6-diazaanonane-1,9-diyl dinitrate (VIIIb). Yield 70%, mp 88°C [3]. ¹H NMR spectrum, δ , ppm: 1.61 m (2H, CCH₂C), 3.54 t (2H, CH₂N, $J = 7.1$ Hz), 3.84 t (2H, CH₂ONO₂, $J = 6.0$ Hz), 4.78 s (1H, NCH₂N).

5,7-Dinitro-5,7-diazaundecane-1,11-diyl dinitrate (VIIIc). Yield 60%, yellow oily substance. ¹H NMR spectrum, δ , ppm: 1.8–1.9 m (4H, CCH₂CH₂C), 3.80 t (2H, NCH₂C, $J = 6.5$ Hz), 4.32 t (2H, CH₂ONO₂, $J = 7.3$ Hz), 4.95 s (1H, NCH₂N). Found, %: C 28.71; H 4.76; N 22.25. C₉H₁₈N₆O₁₀. Calculated, %: C 29.19; H 4.86; N 22.70.

4,6-Dinitro-4,6-diazaanonane-2,9-diyl dinitrate (VIIIId). Yield 65%, mp 97°C [3]. ¹H NMR spectrum, δ , ppm: 1.49 d.d (3H, CH₃, $J = 2.5, -5.9$ Hz), 4.20 m

(2H, NCH₂C), 4.80 m (1H, CHONO₂), 4.84 s (1H, NCH₂N).

Ternary mixtures Ba–Bd and C (general procedure). *a.* Potassium, sodium, or ammonium salt of the corresponding *N*-hydroxyalkylsulfamic acid, 0.033 mol, and 33% aqueous formaldehyde, 3.1 ml, were added to a solution of 0.033 mol of potassium, sodium, or ammonium *N*-methyl- or *N*-hydroxyalkylsulfamate (for mixture C) in 10 ml of water. The mixture was adjusted to pH 6.5 and evaporated on a rotary evaporator at a bath temperature of 80–90°C. IR spectrum of the condensation product, ν , cm⁻¹: 1190–1230 (NSO₃M), 3500–3600 (OH). The product was added under vigorous stirring to a mixture of 97% nitric acid and 95% sulfuric acid (60:40, by volume; 30 ml of the nitrating mixture was taken for 10 g of the condensation product), cooled to –15 to –20°C. The mixture was stirred for 60 min at –15°C, poured into 50 g of an ice–water mixture, and extracted with ethyl acetate (3 × 15 ml). The extract was washed with water (2 × 10 ml), a 3% aqueous solution of sodium carbonate (10 ml), and water again (10 ml), dried over MgSO₄, and evaporated on a rotary evaporator at a bath temperature not exceeding 60°C.

b. Potassium, sodium, or ammonium *N*-methyl- or *N*-hydroxyalkylsulfamate (for mixture C), 10 mmol, potassium, sodium, or ammonium salt of the corresponding *N*-hydroxyalkylsulfamic acid, 10 mmol, and paraformaldehyde, 0.33 g (11 mmol), were added to 100 ml of 94% H₂SO₄ cooled to 10°C. The mixture was stirred for 10 min at 10°C, cooled to –10 to –15°C, and added to 15 ml of 97% HNO₃ cooled to the same temperature. The mixture was stirred for 60 min at –10 to –15°C, poured into 50 ml of an ice–water mixture, and extracted with chloroform (3 × 20 ml). The extract was washed with water (10 ml), a 3% aqueous solution of sodium carbonate (2 × 10 ml), and water again (10 ml) and evaporated on a rotary evaporator.

Mixture **Ba.** *a.* Yield 60%, mp 11–15°C; composition, mol %: **VI:VIIa:VIIIa** = 28:52:20.

b. Yield 52%; composition, mol %: **VI:VIIa:VIIIa** = 14:74:12.

Mixture **Bb.** *a.* Yield 75%, mp 0–8°C; composition, mol %: **VI:VIIb:VIIIb** = 30:51:19.

b. Yield 60%; composition, mol %: **VI:VIIb:VIIIb** = 31:52:17.

Mixture **Bc.** *a.* Yield 59%, mp –20°C; composition, mol %: **VI:VIIc:VIIIc** = 32:51:17.

b. Yield 55%; composition, mol %: **VI:VIIc:VIIIc** = 28:60:12.

Mixture **Bd.** *a.* Yield 68%, mp 12–17°C; composition, mol %: **VI:VIIId:VIIIId** = 32:50:18.

b. Yield 50%; composition, mol %: **VI:VIIId:VIIIId** = 31:59:10.

Mixture **C.** *a.* Yield 70%, mp 28–34°C; composition, mol %: **VIIIa:IX:VIIIb** = 25:51:24.

b. Yield 56%; composition, mol %: **VIIIa:IX:VIIIb** = 31:52:17.

REFERENCES

1. US Patent no. 391901, 1983; *Chem. Abstr.*, 1983, vol. 98, no. 163 392.
2. Russian Patent no. 2 148 574, 2000; *Chem. Abstr.*, 2002, vol. 136, no. 70676.
3. Tartakovskii, V.A., Ermakov, A.S., Sigai, N.V., and Varfolomeeva, O.N., *Izv. Ross. Akad. Nauk, Ser. Khim.*, 2000, p. 1085.
4. Gafarov, A.N. and Punegova, G.N., *Zh. Org. Khim.*, 1981, vol. 17, p. 716.