

SHORT COMMUNICATIONS

Synthesis of Azido Derivatives of *N,N'*-Dialkyl-*N,N'*-dinitromethanedi- amines and Ternary Mixtures Based Thereon

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Received December 22, 2005

DOI: 10.1134/S1070428007030244

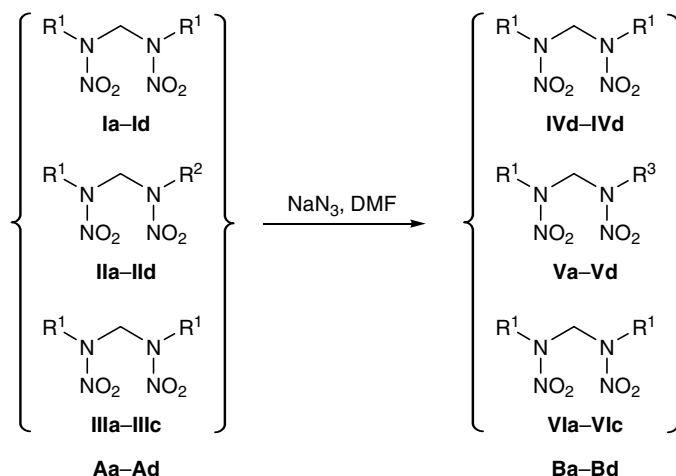
In the recent years, much attention is given to the development of practical methods of synthesis and studies on properties of energy-rich plasticizers for gas-generating compositions. Such plasticizers may be various liquid and low-melting compounds containing energy-rich groups. Although numerous compounds of this sort are known, the problem of searching for new energy-rich plasticizer remains fairly urgent, taking into account quite complex and often contradictory requirements imposed on gas-generating compositions.

We previously developed methods for the preparation of nitrooxy derivatives of *N,N'*-dialkyl-*N,N'*-dinitromethanedi-
amines [1, 2] and mixtures based thereon, which can be used as plasticizers for gas-generating compositions. It is known that replacement of

a nitrooxy group by azido generally leads to reduction of the melting point. Therefore, we expected that replacement of nitrooxy groups in components of the above mixtures will give rise to compositions with lower melting points, higher enthalpy of formation, and improved plasticizing properties.

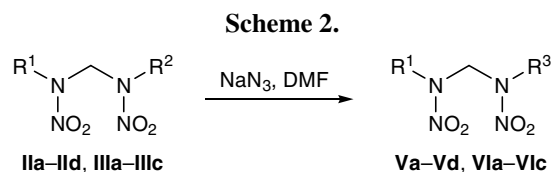
New mixed plasticizers were obtained by azidation of mixtures **Aa–Ad** composed of *N,N'*-dialkyl-*N,N'*-dinitromethanedi-
amines containing nitrooxy groups [3] with sodium azide in dimethylformamide in the presence of CaCl_2 (Scheme 1). Depending on the substituents in the initial components, the reaction temperature and time varied from 80 to 90°C and from 4 to 10 h, respectively. The yields of ternary mixtures **IV–VI** ranged from 60 to 80%. Their composition corre-

Scheme 1.



I, $\text{R}^1 = \text{Me}$ (**a–c**), $\text{O}_2\text{NO}(\text{CH}_2)_2$ (**d**); **II**, $\text{R}^1 = \text{Me}$ (**a–c**), $\text{O}_2\text{NO}(\text{CH}_2)_2$ (**d**), $\text{R}^2 = \text{O}_2\text{NO}(\text{CH}_2)_2$ (**a, d**), $\text{O}_2\text{NO}(\text{CH}_2)_3$ (**b**), $\text{MeCH}(\text{ONO}_2)\text{CH}_2$ (**c**); **III**, $\text{R}^1 = \text{O}_2\text{NO}(\text{CH}_2)_2$ (**a**), $\text{O}_2\text{NO}(\text{CH}_2)_3$ (**b**), $\text{MeCH}(\text{ONO}_2)\text{CH}_2$ (**c**); **IV**, $\text{R}^1 = \text{Me}$ (**a–c**), $\text{N}_3(\text{CH}_2)_2$ (**d**); **V**, $\text{R}^1 = \text{Me}$ (**a–c**), $\text{N}_3(\text{CH}_2)_2$ (**d**), $\text{R}^3 = \text{N}_3(\text{CH}_2)_2$ (**a, d**), $\text{N}_3(\text{CH}_2)_3$ (**b**), $\text{MeCH}(\text{N}_3)\text{CH}_2$ (**c**); **VI**, $\text{R}^1 = \text{N}_3(\text{CH}_2)_2$ (**a**), $\text{N}_3(\text{CH}_2)_3$ (**b**), $\text{MeCH}(\text{N}_3)\text{CH}_2$ (**c**).

sponded to the composition of initial mixtures **Aa–Ad**. It was determined by ^1H NMR spectroscopy from the intensities of proton signals from the methylene groups located between the nitroamino groups. To identify particular components of the obtained ternary mixtures, we synthesized individual azido-substituted *N,N'*-dialkyl-*N,N'*-dinitromethanediamines according to the procedures reported in [4, 5] (Scheme 2).



The results of our studies showed that mixtures on the basis of azido-substituted *N,N'*-dialkyl-*N,N'*-dinitromethanediamines melt at a lower temperature ($<0^\circ\text{C}$) than the initial nitroxy derivatives.

Azidodinitrodiazaalkanes Va and Vc (general procedure). Calcium chloride, 40 mmol, was added to a solution of 20 mmol of the corresponding nitrooxy-dinitrodiazaalkane in 40 ml of DMF, and the mixture was stirred for 30 min at 90°C . Sodium azide, 60 mmol, was then added, and the mixture was stirred for a specified time at a required temperature. The mixture was poured into 500 ml of water and extracted with benzene (5×50 ml), the extracts were washed with water (5×50 ml), dried over MgSO_4 , and evaporated on a rotary evaporator, and the residue was washed with diethyl ether.

1-Azido-3,5-dinitro-3,5-diazaheptane (Va). Azidation temperature 90°C (3 h). Yield 79%, mp $34.5\text{--}35.5^\circ\text{C}$. IR spectrum, ν , cm^{-1} : 1290, 1540, 1560 (N--NO_2); 2120 (N_3). ^1H NMR spectrum, δ , ppm: 3.40 s (3H, CH_3N), 3.65 t (2H, CH_2N_3 , $J = 2.45$ Hz), 3.95 t (2H, CH_2NNO_2 , $J = 3.67$ Hz), 5.66 s (2H, NCH_2N). Found, %: C 22.06; H 4.26; N 44.25. $\text{C}_4\text{H}_9\text{N}_7\text{O}_4$. Calculated, %: C 21.92; H 4.11; N 44.70.

2-Azido-4,6-dinitro-4,6-diazaheptane (Vc). Azidation temperature $85\text{--}90^\circ\text{C}$ (8 h). Yield 81%, mp 15°C . IR spectrum, ν , cm^{-1} : 1290, 1455, 1530 (N--NO_2); 2100 (N_3). ^1H NMR spectrum, δ , ppm: 1.45 d (3H, CH_3CH , $J = 6.5$ Hz), 3.55 s (3H, CH_3N), 3.88 d.d (1H, NCH_2CH , $J = 6.8$ Hz), 4.15 m (2H, NCH_2CH), 5.78 s (2H, NCH_2N). Found, %: C 25.97; H 4.82. $\text{C}_5\text{H}_{11}\text{N}_7\text{O}_4$. Calculated, %: C 25.75; H 4.72.

Diazidodinitrodiazaalkanes VIa–VIc were synthesized as described above for compounds **Va** and **Vc** from symmetric dinitrooxydinitrodiazaalkanes.

1,7-Diazido-3,5-dinitro-3,5-diazaheptane (VIa). Azidation temperature 90°C (4 h). Yield 70%,

mp 32°C [6]. ^1H NMR spectrum, δ , ppm: 2.7 t (4H, CH_2N_3 , $J = 5.6$ Hz), 4.49 t (2H, NCH_2C , $J = 5.6$ Hz), 5.6 s (2H, NCH_2N).

1,9-Diazido-4,6-dinitro-4,6-diazaanonane (VIb). Azidation temperature 95°C (5 h). Yield 95%, mp 27°C . IR spectrum, ν , cm^{-1} : 1295, 1465, 1565 (N--NO_2); 2110 (N_3). ^1H NMR spectrum, δ , ppm: 1.61 m (4H, CCH_2C), 3.58 t (4H, CH_2N_3 , $J = 2.5$ Hz), 3.89 t (4H, CH_2N , $J = 3.7$ Hz), 5.8 s (2H, NCH_2N). Found, %: C 84.10; H 14.14. $\text{C}_7\text{H}_{14}\text{N}_{10}\text{O}_4$. Calculated, %: C 84.07; H 14.11.

2,8-Diazido-4,6-dinitro-4,6-diazaanonane (VIc). The azidation was performed for 12 h at $85\text{--}90^\circ\text{C}$ and for 20 min at 140°C . Yield 69%, mp 40°C . IR spectrum, ν , cm^{-1} : 1290, 1440, 1550 (N--NO_2); 2120 (N_3). ^1H NMR spectrum, δ , ppm: 1.42 d (6H, CH_3CH , $J = 6.5$ Hz), 3.90 d.d (2H, NCH_2CH , $J = 6.8$ Hz), 4.20 m (4H, NCH_2CH), 5.81 s (2H, NCH_2N). Found, %: N 46.71. $\text{C}_7\text{H}_{14}\text{N}_{10}\text{O}_4$. Calculated, %: N 46.34.

Ternary mixtures Ba–Bd were obtained following the procedure described above for azidodinitrodiazaalkanes **Va** and **Vc** using the corresponding ternary mixture **Aa–Ad** as substrate.

Ternary mixture Ba. Composition of **Aa**, mol %: **Ia:IIa:IIIa** = 25:50:25. Azidation temperature 90°C (4 h). Yield 78%, mp $\leq 0^\circ\text{C}$; composition, mol %: **IVa:Va:VIa** = 26:50:24.

Ternary mixture Bb. Composition of **Ab**, mol %: **Ib:IIb:IIIb** = 3:20:77. Azidation temperature 90°C (6 h). Yield 81, mp $\leq -10^\circ\text{C}$; composition, mol %: **IVb:Vb:VIb** = 4:20:76.

Ternary mixture Bc. Composition of **Ac**, mol %: **Ic:IIc:IIIc** = 25:50:25. Azidation temperature 90°C (10 h). Yield 68%, mp $\leq 0^\circ\text{C}$; composition, mol %: **IVc:Vc:VIc** = 27:51:22.

Ternary mixture Bd. Composition of **Ad**, mol %: **Id:IIId:IIIId** = 25:51:24. Azidation temperature 90°C (5 h). Yield 70%, mp $\leq 0^\circ\text{C}$; composition, mol %: **IVd:Vd:VIId** = 25:51:24.

The IR spectra were recorded in KBr on a Specord M-80 spectrometer. The ^1H NMR spectra were obtained on a Bruker AC-300 spectrometer at 300.13 MHz using $(\text{CD}_3)_2\text{CO}$ as solvent and hexamethyldisiloxane as internal reference.

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