Synthesis of *N*-(3-azido-2-nitroxypropyl)-, *N*-(2,3-diazidopropyl)-, and *N*-(2-azido-3-methoxypropyl)-*N*-alkylnitramines

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N-(3-Azido-2-nitroxypropyl)-*N*-alkylnitramines and *N*-(2,3-diazidopropyl)-*N*-alkylnitramines were prepared by nitration and azidation of *N*-alkyl-*N*-(2-hydroxy-3-chloropropyl)sulfamates and *N*-(3-azido-2-hydroxypropyl)-*N*-alkylsulfamates.

Key words: *N*-alkylsulfamates, epichlorohydrin, glycidol ethers, *N*-(3-azido-2-hydroxypropyl)-*N*-alkylsulfamates, *N*-(3-azido-2-nitroxypropyl)-*N*-alkylnitramines, *N*-(2,3-diazidopropyl)-*N*-alkylnitramines.

As part of our continuing systematic studies of procedures for the preparation of nitrogen- and nitrogen-oxygen-containing polyfunctional aliphatic compounds, we have considered the synthesis of derivatives of 2-nitroxy- and 2-azidopropyl-*N*-alkynylnitramines.[1—3] In this work, we studied the synthesis of diazido and azidonitroxy derivatives of *N*-nitramines (Scheme 1). *N*-Alkyl-*N*-(2-hydroxy-3-chloropropyl)sulfamates were used as starting compounds, which were transformed into the target products according to two procedures. The first procedure (method *A*) involved prior azidation of *N*-alkyl-*N*-(2-hydroxy-3-chloropropyl)sulfamates (**1**), which have been prepared previously,[1,2] to the corresponding *N*-(3-azido-2-hydroxypropyl)-*N*-alkylsulfamates (**2**). This reaction proceeded with ~90% yield (the ^{1}H NMR spectra of sulfamates **2** are given in Table 1). Compounds **2** (without additional purification) were subjected to nitration with an acetic anhydride—HNO_3 mixture to form *N*-(3-azido-2-nitroxypropyl)-*N*-alkylnitramines (**3**) in 65—70% yields. Azidation of compounds **3** under standard conditions afforded 2,3-diazidopropyl-*N*-alkylnitramines (**5**) in 40—55% yields. The second procedure (method *B*) involved nitration of compounds **1** to form *N*-alkyl-*N*-(3-methoxy- and 3-chloro-2-nitroxypropyl)nitramines (**4**) in 70—80% yields. Then, we performed azidation of compounds **4** with sodium azide in DMF to obtain *N*-(2-azido-3-methoxypropyl)- and *N*-(2,3-diazidopropyl)-*N*-alkylnitramines (**5**) in 25—39% yields. The degree of replacement of the nitrate group by the azide group was detected by IR spectroscopy ($\nu(-ONO_2)$ 1680 cm^{-1} and $\nu(-N_3)$ 2125 cm^{-1}).

The resulting compounds (**2**, **3**, and **5**) were characterized by ^{1}H NMR and IR spectroscopy and elemental analysis (Tables 1—3). These compounds are of interest as active plasticizers in gas-producing compositions. The yields of compounds **5** prepared according to method *A* were somewhat higher than those obtained by method *B*. Therefore, the former procedure for the synthesis is somewhat preferred.

Experimental

The ^{1}H NMR spectra (δ) were recorded on Bruker WM-250 and Bruker AM-300 instruments (250 and 300 MHz,

Scheme 1

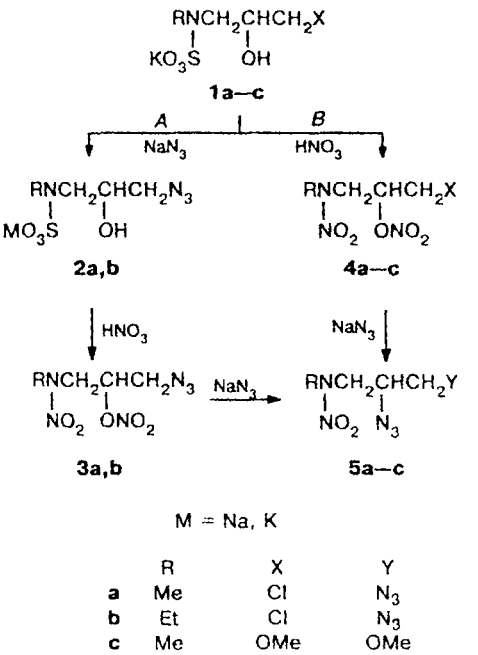

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Table 1. ^{1}H NMR spectra of *N*-(3-azido-2-hydroxypropyl)-*N*-alkylsulfamates (**2**) (in D_2O)

Compound	^{1}H NMR, δ
2a	2.71 (s, 3 H, CH_3N); 2.95 (m, 2 H,NCH_2); 3.40—3.60 (m, 2 H, CH_2N_3); 4.00 (m, 1 H, CHOH)
2b	1.15 (t, 3 H, CH_3); 2.80—3.10 (m, 4 H, CH_2NCH_2); 3.40—3.60 (m, 2 H, CH_2N_3); 4.00 (m, 1 H, CHOH)

respectively) in D_2O, $(CD_3)_2CO$, and $CDCl_3$ with HMDS as the internal standard. The products were purified by recondensation using an apparatus for sublimation.

Potassium sodium salt of *N*-(3-azido-2-hydroxypropyl)-*N*-ethylsulfaminic acid (2b). NaN_3 (2 g) was added to a solution of potassium *N*-(2-hydroxy-3-chloropropyl)-*N*-ethylsulfamate (**1b**) (4 g) in anhydrous DMF (15 mL) at 100—105 °C. The reaction mixture was stirred for 10 h and then concentrated. The product was extracted with hot EtOH (2×20 mL). The reaction mixture was concentrated. The mixed potassium sodium salt of *N*-(3-azido-2-hydroxypropyl)-*N*-ethylsulfaminic acid (**2b**) was obtained in a yield of 3.71 g. Salt **2a** was prepared analogously.

***N*-(3-Azido-2-nitroxyporpyl)-*N*-ethylnitramine (3b).** Potassium sodium salt **2b** (3.34 g) was gradually added to a mixture of Ac_2O (19.3 mL) and 98% HNO_3 (5.5 mL) at the temperature of −7 to −10 °C. The reaction mixture was stirred at −7 to −10 °C for 1 h. Then the mixture was poured into ice water and extracted with ethyl acetate (3×40 mL). The extract was washed with an aqueous solution of Na_2CO_3 and water. The solvent was evaporated. The mixture was purified by recondensation using an apparatus for sublimation at the temperature of the bath of 70—75 °C (0.2 Torr). *N*-(3-Azido-2-nitroxypropyl)-*N*-ethylnitramine (**3b**) was obtained in a yield of 1.71 g. Compound **3a** was prepared analogously.

***N*-(2,3-Diazidopropyl)-*N*-ethylnitramine (5b). Method *A*.** $CaCl_2$ (1.60 g) and NaN_3 (1.19 g) were gradually added to a solution of compound **3b** (1.71 g) in DMF (15 mL) at 80—85 °C. The reaction mixture was stirred for 26 h and poured into H_2O (60 mL). The mixture was filtered. The filtrate was extracted with benzene (4×35 mL). The benzene solution was washed with water and concentrated. *N*-(2,3-Diazidopropyl)-*N*-ethylnitramine (**5b**) was obtained in a yield of 0.63 g. The resulting compound was purified by recondensation at 70—75 °C (0.2 Torr). Compound **5a** was prepared analogously.

***N*-(2-Azido-3-methoxypropyl)-*N*-methylnitramine (5c). Method *B*.** $CaCl_2$ (1.27 g) and NaN_3 (0.75 g) were gradually added to a solution of *N*-(3-methoxy-2-nitroxy)-*N*-methylnitramine **4c** (1.20 g), which was prepared previously,[2] in DMF (15 mL) at 85—90 °C. The reaction mixture was stirred for 30 h and poured into H_2O (50 mL). The mixture was filtered, the filtrate was extracted with benzene (4×30 mL), and the benzene solution was washed with water and concentrated. *N*-(2-Azido-3-methoxypropyl)-*N*-methylnitramine (**5c**) was obtained in a yield 0.42 g. The resulting compound was purified by recondensation at 60—65 °C (0.2 Torr). Compounds **5a,b** were prepared analogously but the temperature was maintained at 80—85 °C. The duration of the reaction was 26 h.

Table 2. Characteristics of *N*-(3-azido-2-nitroxypropyl)-*N*-alkylnitramines, *N*-(2,3-diazidopropyl)-*N*-alkylnitramines, and *N*-(2-azido-3-methoxypropyl)-*N*-alkylnitramines

Compound	Yield (%)	M.p./°C [n_D^{22}]	Found / Calculated (%) C	H	N	Molecular formula
3a	67	59—60	22.56 / 21.82	3.59 / 3.66		$C_4H_8N_6O_5$
3b	63	[1.5017]	26.08 / 25.65	4.25 / 4.30	36.25 / 35.89	$C_5H_{10}N_6O_5$
5a	55[a] 25[b]	[1.5215]	24.26 / 24.00	4.13 / 4.03	56.46 / 55.98	$C_4H_8N_8O_2$
5b	40[a] 26[b]	[1.5180]			52.12 / 52.32	$C_5H_{10}N_8O_2$
5c	39	[1.4940]	32.15 / 31.75	5.97 / 5.86	37.12 / 37.02	$C_5H_{11}N_5O_3$

[a] Azidation of compound **3**.
[b] Azidation of compound **4**.

Table 3. ^{1}H NMR spectra of *N*-(3-azido-2-nitroxypropyl)-*N*-alkylnitramines, *N*-(2,3-diazidopropyl)-*N*-alkylnitramines, and *N*-(2-azido-3-methoxypropyl)-*N*-alkylnitramines

Compound	^{1}H NMR, δ
3a*	3.48 (s, 3 H, CH_3N); 3.87 (m, 2 H, CH_2N_3); 4.22 (m, 2 H, NCH_2); 5.65 (m, 1 H, $CHONO_2$)
3b	1.20 (t, 3 H, CH_3C); 3.50—3.75 (m, 4 H, CH_2N_3, CH_2N); 4.00 (m, 2 H, NCH_2); 5.48 (m, 1 H, $CHONO_2$)
5a	3.48 (s, 3 H, CH_3N); 3.50 (m, 2 H, CH_2N_3); 3.80 (m, 2 H, NCH_2); 4.08 (m, 1 H, CHN_3)
5b	1.21 (t, 3 H, CH_3C); 3.32—3.92 (m, 6 H, CH_2N_3, CH_2NCH_2); 4.02 (m, 1 H, CHN_3)
5c	3.38 (s, 3 H, OCH_3); 3.47 (s, 3 H, CH_3N); 3.55 (m, 2 H, CH_2O); 3.80 (m, 2 H, NCH_2); 4.08 (m, 1 H,CHN_3)

* The spectrum of compound **3a** was measured in deuteroacetone and the remaining spectra were measured in $CDCl_3$.

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