Synthesis and nitration of condensation products of sulfamates with aliphatic amines and formaldehyde

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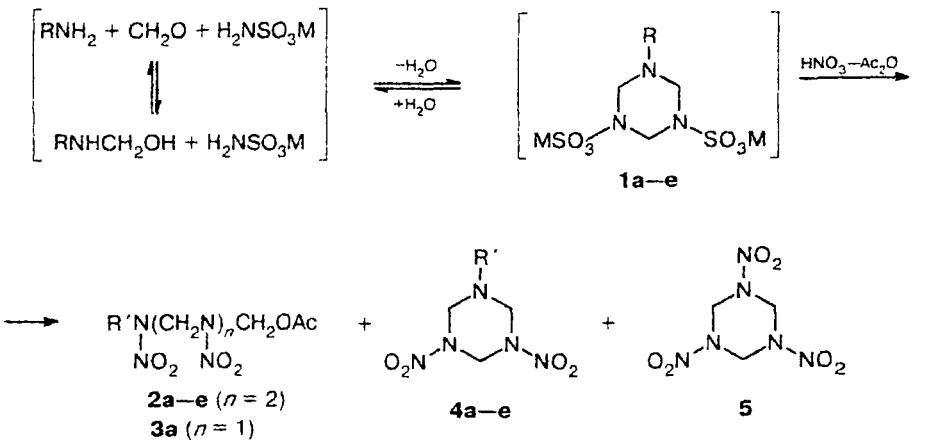
A method for the synthesis of 5-alkyl-1,3-dinitro-1,3,5-triazacyclohexanes and linear polynitramines was proposed. It includes the reaction of aliphatic amines with sulfamates and formaldehyde and nitration of the reaction products. The yield and composition of nitramino derivatives depend on the conditions of the condensation and nitration.

Key words: aliphatic amines, nitramino derivatives, sulfamates.

Previously, reactions of derivatives of sulfamic acid with formaldehyde and compounds containing a mobile H atom (ureas, guanidine, *gem*-dinitroalkanes, and aminofurazans) were studied.[1–4] Using the Mannich reaction products for the synthesis of nitramino derivatives, we investigated the reaction of sulfamic acid salts with formaldehyde and aliphatic amines and subsequent nitration of the resulting products. The condensation of aliphatic amines with formaldehyde and sulfamates was carried out in an aqueous or aqueous-ethanolic solution at pH 6.5–7.0. After evaporation of water, crystalline products **1a–e** were obtained. Their IR spectra indicated the presence of $N-SO_3M$ groups (~1200 cm^{-1}) and almost complete absence of NH and OH groups at 3200–3600 cm^{-1}, probably, due to a polymeric or cyclic structure of **1**. Products **1** could hardly be identified because of their decomposition during purification. For this reason, as in other cases,[1,2] products **1** were nitrated with an HNO_3-Ac_2O mixture without additional purification (Scheme 1).

As a result, the nitration of a condensation product with methylamine gave 1-acetoxy-2,4,6-trinitro-2,4,6-triazaheptane (**2a**) and 1-methyl-3,5-dinitro-1,3,5-triazacyclohexane (**4a**). In addition, 1-acetoxy-2,4-dinitro-2,4-diazapentane (**3a**) and hexogen (**5**)

Scheme 1



M = K, Na

	a	b	c	d	e
R	Me	Et	Bu	$(CH_2)_2OH$	$(CH_2)_3OH$
R'	Me	Et	Bu	$(CH_2)_2ONO_2$	$(CH_2)_3ONO_2$

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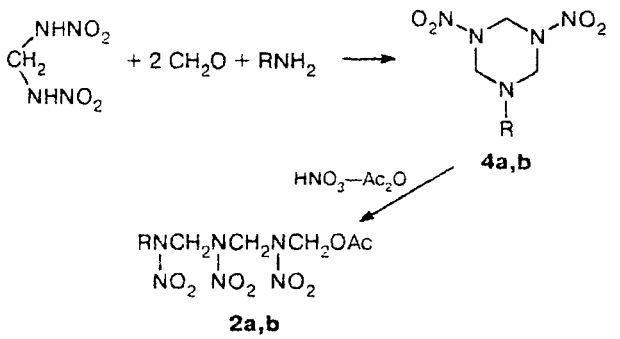
(^{1}H NMR, δ: 6.24) were detected as admixtures (both ~5%).

Earlier,[5,6] compounds **2a,b** and **4a,b** were obtained by condensation of methylenedinitramine with formaldehyde and alkylamines (Scheme 2).

Scheme 2



The yields of compounds **4a,b** were 40—60%. The nitrolysis of the ring in **4a,b** with an HNO_3—Ac_2O mixture occurred in ~70—80% yield. However, the use of explosive and chemically unstable methylenedinitramine limits the applicability of this method.

The presence of compounds **4a** and **2a** (resulting from nitrolysis of the former) in the nitration products obtained by the method proposed suggests that the reaction of methylamine with potassium sulfamate and formaldehyde results in dipotassium 1-methyl-1,3,5-triazacyclohexane-3,5-disulfonate **1a**. The yields and ratio of products **2** and **4** mainly depend on the ratio of the components of the nitrating mixture and the ratio of the starting reagents (Table 1). Similar results were obtained with other aliphatic amines, *viz.*, ethylamine, *n*-butylamine, ethanolamine, and 3-aminopropan-1-ol (Table 2). The method proposed here for the preparation of compounds **2** and **4** is comparable with the known one in product yield,[5,6] but its advantage lies in the use of available chemicals. However, the nitration of the reaction products of sulfamates with ethylenediamine or 1,4-diaminobutane afforded only linear polynitraza compounds (**6** or **7**); cyclic nitramino derivatives could not be isolated (Scheme 3).

Table 1. Dependence of the yield of nitramines **2** and **4** on the conditions of the nitration and condensation

pH in the condensation	$MeNH_2$: H_2NSO_3K: CH_2O	HNO_3/Ac_2O /mol mol^{-1}	Yield (%)	
			2a	**4a**
5.0	1 : 2 : 3	0.6*	20	1
6.0	1 : 2 : 3	0.6*	33	3
6.5	1 : 2 : 3	0.6*	39	4
7.0	1 : 2 : 3	0.6*	36	4
8.0	1 : 2 : 3	0.6*	12	1
6.5	1 : 2 : 3	6**	10	33
6.5	2 : 3 : 2	6**	12	17
6.5	1 : 1 : 2	6**	6	12

* At 10—15 °C.
** At −5 to 0 °C.

Table 2. Physicochemical properties of nitramines **2**, **4**, **6**—**9**

Compound	Yield (%)	M.p. /°C	Found / Calculated (%) C	H	N	Molecular formula
2b	38	133 [5]				
2c	35	116			24.61 24.84	$C_9H_{18}N_6O_8$
2d	48	116	23.04 22.65	3.68 3.53	26.04 26.41	$C_7H_{13}N_7O_{11}$
2e	45	102			25.84 25.46	$C_8H_{15}N_7O_{11}$
4b	30	96 [5]				
4c	25	85			29.98 30.03	$C_7H_{15}N_5O_4$
4d	41	84			31.80 31.57	$C_5H_{10}N_6O_7$
4e	36	82			25.23 25.72	$C_6H_{12}N_6O_7$
6a	20	206	24.65 24.41	4.01 3.76	27.96 28.47	$C_{12}H_{22}N_{12}O_{16}$
6b	23	223	27.84 27.19	3.96 4.24	26.65 27.16	$C_{14}H_{26}N_{12}O_{16}$
7a	31	103	26.71 27.16	3.86 4.10		$C_{10}H_{18}N_8O_{12}$
7b	36	97	30.42 30.64	4.53 4.71	24.33 23.83	$C_{12}H_{22}N_8O_{12}$
8a	82	183			32.17 32.89	$C_8H_{16}N_{14}O_{18}$
8b	78	165	19.85 19.24	3.29 3.23		$C_{10}H_{20}N_{14}O_{18}$
9	45	123	20.60 20.26	3.20 2.98	29.43 29.53	$C_4H_7N_5O_7$

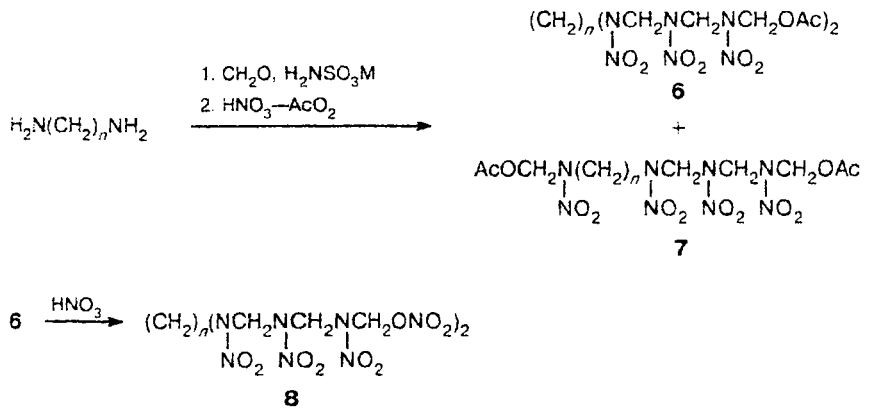
With the aim of obtaining a nitrate-containing analog of hexogen, we studied the condensation of 1,3-diaminopropan-2-ol (**10a**) and its derivatives (**10b,c**) with formaldehyde (Scheme 4).

Satisfactory results were obtained only with sulfo derivatives **10b,c** synthesized according to a procedure similar to the known one.[7] Thus, the nitration of the reaction product of potassium *N*-(3-amino-2-hydroxypropyl)sulfamate (**10b**) with formaldehyde gave compound **9** in 32% yield. The yield of the latter increases to 42% upon nitrating the product obtained in the reaction of dipotassium 2-hydroxypropane-1,3-disulfamate (**10c**) with formaldehyde. Note that compound **9** is also formed in the nitration of the reaction product of 1,3-diaminopropan-2-ol with formaldehyde, though in lower yield (~6—8%).

Experimental

^{1}H NMR spectra were recorded on a Bruker WM-250 instrument (250.13 MHz) in acetone-d_6 with HMDS as the internal standard. IR spectra were recorded on a UR-20 instrument (pellets with KBr).

Scheme 3

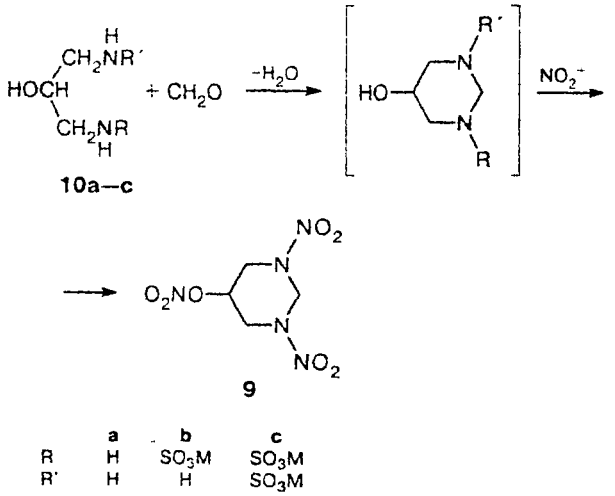


6, 7, 8: n = 2 (**a**), 4 (**b**)

The yields and characteristics of the products are presented in Table 2. ^{1}H NMR and IR spectral parameters are given in Table 3.

1-Acetoxy-2,4,6-trinitro-2,4,6-triazaheptane (2a). A 25% aqueous solution of methylamine (1.25 mL, 10 mmol) and 32% formalin (2.7 mL, 30 mmol) were added to a solution of potassium sulfamate (2.7 g, 20 mmol) in 6 mL of water. The reaction mixture was adjusted to pH 6.5 (with HCl or KOH) and concentrated *in vacuo* at 80—90 °C. The residue (**1a**, 3.36 g, m.p. (decomp.) ~176—180 °C) was added to a mixture of Ac_2O (12 mL, 120 mmol) and 98% HNO_3 (3.5 mL, 75 mmol) at 8—10 °C. The resulting solution was stirred at 20—25 °C for 30 min and then poured into 60 mL of water with ice. The crystalline product that formed was filtered off, washed successively with water, 3% Na_2CO_3, and water, dried, and recrystallized from ethanol to give compound **2a** (1.16 g, 39%), m.p. 155 °C (*cf.* Ref. 6: m.p. 154—155 °C). The filtrate was extracted with AcOEt (3×20 mL). The extract was successively washed with water, 3% Na_2CO_3, and water and concentrated.

Scheme 4



	a	b	c
R	H	SO_3M	SO_3M
R'	H	H	SO_3M

The residue was recrystallized from aqueous ethanol to give 1-methyl-3,5-dinitro-1,3,5-triazacyclohexane (0.09 g, ~4%) (**4a**), m.p. 105 °C (*cf.* Ref. 5: m.p. 104 °C). Compounds **2b—e** and **4b—e** were obtained in a similar way.

2,4,6,9,11,13-Hexanitro-1,14-dinitroxy-2,4,6,9,11,13-hexaazatetradecane (8a). A 30% solution of formaldehyde (9.60 mL, 110 mmol) was added to a solution of ethylenediamine (1.02 g, 17 mmol) and potassium sulfamate (8.64 g, 64 mmol) in 20 mL of water. The reaction mixture was adjusted to pH 6.7 (with HCl or KOH) and concentrated *in vacuo* at ~80—90 °C. The residue (10.72 g, m.p. (decomp.) 190—195 °C) was added to a mixture of Ac_2O (40 mL, 400 mmol) and 98% HNO_3 (10.6 mL, 250 mmol) at 0—5 °C. The resulting solution was stirred at 40 °C for 60 min and then poured into 100 g of water with ice. The precipitate that formed was filtered off, washed with water, and recrystallized from acetone to give 1,14-diacetoxy-2,4,6,9,11,13-hexanitro-2,4,6,9,11,13-hexaazatetradecane (**6a**) (1.79 g), m.p. 205—207 °C. The filtrate was extracted with AcOEt (3×30 mL). The extract was washed with water (1×10 mL), combined with the mother liquor formed upon recrystallization of **6a**, and concentrated. The residue was recrystallized from Pr^iOH to give 1,10-diacetoxy-2,4,6,9-tetranitro-2,4,6,9-tetraazadecane (**7a**) (3.12 g), m.p. 103—104 °C. Compound **6** (1 g) was added at −10 to −15 °C to 3 mL of 98% HNO_3. The reaction mixture was stirred until complete dissolution and poured into ice. The precipitate that formed was filtered off, washed with water three times, and dried over P_2O_5. The yield of compound **8a** was ~0.84 g, m.p. 182—183 °C. Analogously, 1,16-diacetoxy-2,4,6,11,13,15-hexanitro-2,4,6,11,13,15-hexaazahexadecane (**6b**), 1,12-diacetoxy-2,4,6,11-tetranitro-2,4,6,11-tetraazadodecane (**7b**), and 2,4,6,11,13,15-hexanitro-1,16-dinitroxy-2,4,6,11,13,15-hexaazahexadecane (**8b**) were synthesized.

3,5-Dinitro-1-nitroxy-3,5-diazacyclohexane (9). Method *A* (from **10b**). A solution of potassium *N*-(2-hydroxy-3-chloropropyl)sulfamate[7] (2.50 g, 11 mmol) in 21% ammonium hydroxide (35 mL, 410 mmol) was kept at 45 °C for 15 h. KOH (0.56 g, 10 mmol) was added, and the reaction mixture was concentrated. Then, the product was dissolved in ~20 mL of water, 30% formalin (1.02 g, 10 mmol) was added, and pH was adjusted to ~6.5 (with HCl or KOH). The resulting solution was concentrated *in vacuo* at 90—100 °C. The residue was added to a mixture of Ac_2O (13.6 mL, 136 mmol), 98% HNO_3 (3.4 mL,

Table 3. ^{1}H NMR and IR spectral data for nitramines **2**, **4**, and **6—9**

Compound	IR, ν/cm^{-1}	^{1}H NMR, δ (*J*/Hz)
2c	1283, 1540—1588 (NNO_2); 1755 (OAc)	0.8—1.5 (m, 7 H, $MeCH_2CH_2$); 2.04 (s, 3 H, MeCO); 4.05 (t, 2 H, CH_2N); 5.81 (s, 4 H, 2 NCH_2N); 5.90 (s, 2 H, NCH_2OAc)
2d	1282, 1540—1568, 1591 (NNO_2); 1756; ONO_2 1646 (OAc)	2.04 (s, 3 H, MeCO); 4.46 (t, 2 H, $CH_2\underline{CH_2}N$, J = 5.5); 4.88 (t, 2 H, CH_2ONO_2, J = 5.0); 5.84 (s, 4 H, 2 NCH_2N); 5.93 (s, 2 H, $N\underline{CH_2}OAc$)
2e	1279, 1540—1590 (NNO_2); 1754; ONO_2 1637 (OAc)	2.03 (s, 3 H, MeCO); 2.20 (m, 2 H, $CH_2\underline{CH_2}CH_2N$); 4.12 (t, 2 H, $CH_2\underline{CH_2}N$, J = 6.0); 4.68 (t, 2 H, CH_2ONO_2, J = 5.5); 5.81 (s, 4 H, 2 NCH_2N); 5.92 (s, 2 H, $N\underline{CH_2}OAc$)
4c	1280, 1536, 1560, 1578 (NNO_2)	
4d	1281, 1540—1585 (NNO_2); 1648 (ONO_2)	4.41 (t, 2 H, $CH_2\underline{CH_2}N$, J = 5.5); 4.89 (t, 2 H, CH_2ONO_2, J = 5.0); 5.37 (s, 2 H, NCH_2N); 5.96 (s, 4 H, 2 CH_2N)
4e	1280, 1540—1583 (NNO_2); 1642 (ONO_2)	2.16 (m, 2 H, $CH_2\underline{CH_2}CH_2N$); 4.30 (t, 2 H, $CH_2\underline{CH_2}N$, J = 6.5); 4.68 (t, 2 H, CH_2ONO_2, J = 5.5); 5.38 (s, 2 H, NCH_2N); 5.89 (s, 4 H, 2 CH_2N)
6a	1288, 1560—1570 (NNO_2); 1760 (OAc)	
6b	1280, 1560—1580 (NNO_2); 1760 (OAc)	1.70 (m, 4 H, $NCH_2\underline{CH_2}\underline{CH_2}CH_2N$); 2.01 (s, 6 H, 2 MeCO); 3.95 (m, 4 H, 2 $CH_2\underline{CH_2}N$); 5.73 (s, 4 H, 2 CH_2N); 5.87 (s, 4 H, 2 NCH_2N); 5.96 (s, 4 H, 2 NCH_2OAc)
7a	1275—1280, 1560—1575 (NNO_2); 1758 (OAc)	2.05 (s, 6 H, $2CH_3CO$); 3.95 (m, 4 H, $N\underline{CH_2}\underline{CH_2}N$); 5.70 (s, 4 H, 2 NCH_2N); 5.82 (s, 2 H, NCH_2CO); 5.93 (s, 2 H, NCH_2CO)
7b	1270—1280, 1560—1580 (NNO_2); 1750 (OAc)	
8a	1280—1290, 1570—1580 (NNO_2); 1670 (ONO_2)	3.92 (m, 4 H, NCH_2CH_2N); 5.71 (s, 4 H, 2 NCH_2N); 5.80 (s, 4 H, 2 NCH_2N); 6.10 (s, 4 H, $2NCH_2ONO_2$)
8b	1270—1282, 1560—1580 (NNO_2); 1675 (ONO_2)	1.72 (m, 4 H, $NCH_2\underline{CH_2}\underline{CH_2}CH_2N$); 3.95 (m, 4 H, 2 CH_2N); 5.70 (s, 4 H, 2 NCH_2N); 5.85 (s, 4 H, 2 NCH_2N); 6.15 (s, 4 H, $2NCH_2ONO_2$)
9	1272, 1552 (NNO_2); 1640, 1648 (ONO_2)	4.25, 5.05 (both d, 4 H, 2 $CH\underline{CH_2}N$, $J_1 = J_2$ = 15.6); 5.82, 7.00 (both d, 2 H, NCH_2N, $J_1 = J_2$ = 15.6); 5.70 (m, 1 H, $CHONO_2$)

80 mmol), and methylamine hydrochloride (0.17 g) at 0—5 °C. The reaction mixture was stirred for 20 min, methylamine hydrochloride (0.17 g) was added, and stirring was continued for an additional 40 min. Then the reaction mixture was poured into 50 mL of water with ice, and the products were extracted with AcOEt (3×20 mL). The extract was washed with water and sodium carbonate. The solution was concentrated, and the product was recrystallized from MeOH to give compound **9** (0.75 g, 32%), m.p. 123 °C, ρ 1.76 g cm^{-3}. The molecular mass of compound **9**, determined by Rast's method, equals 234; calculated: M 237.

Method ***B*** (from **10c**). KOH (0.58 g, 12 mmol) was added at 25—30 °C to potassium *N*-(2-hydroxy-3-chloropropyl)-sulfamate (3 g, 13 mmol) in 8 mL of water. After 1 h, potassium sulfamate (1.78 g, 13 mmol) was added. The reaction mixture was kept at ~70 °C for 45 h and then concentrated *in vacuo*. A 30% aqueous solution of formaldehyde (1.25 g, 12 mmol) was added to the resulting potassium 2-hydroxypropane-1,3-disulfamate in 20 mL of water. The reaction mixture was adjusted to pH ~6.5 (with HCl or KOH) and concentrated at 115—125 °C. The condensation product was added to a mixture of 88% H_2SO_4 (5 mL) and 98% HNO_3 (7 mL) at −13 to −17 °C, stirred for 1 h, and then poured into 50 mL of water with ice. The products were extracted with AcOEt (3×20 mL). The extract was washed with water and 3% Na_2CO_3 and concentrated. The residue was recrystallized from MeOH to give compound **9** (1.31 g, 42%).

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