Organic Chemistry

Synthesis of *N,N'*-dialkylmethylenebis(nitramines) from *N*-alkylsulfamates

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Symmetrical and unsymmetrical *N,N'*-dialkylmethylenebis(nitramines) were obtained from *N*-alkylsulfamates by condensation with formaldehyde and subsequent nitration.

Key words: symmetrical and unsymmetrical *N,N'*-dialkylmethylenebis(nitramines), *N*-alkylsulfamates, *N*-alkylnitramines.

N,N'-Dialkylmethylenebis(nitramines) possess the properties of plasticizers for gas-evolving compositions, which necessitates the development of new approaches to their synthesis.

There are several methods for the preparation of *N,N'*-dialkylmethylenebis(nitramines). The most convenient ones are based on the reactions of primary nitramines with paraform in sulfuric acid.[1,2] However, the use of primary nitramines is limited by the relatively complicated way of their synthesis as well as by their instability.

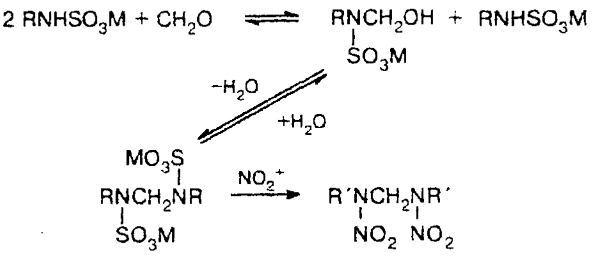
It is known that sulfamic acid derivatives can be involved in the Mannich reaction with formaldehyde and compounds bearing a mobile hydrogen atom.[3,4]

One can assume that, under certain conditions, *N*-alkylsulfamates can also condense with themselves and formaldehyde.

Indeed, the reaction carried out in an aqueous or aqueous-ethanolic medium yields *N,N'*-methylenebissulfamates **1a—f** and, following nitration of the latter, *N,N'*-dialkylmethylenebis(nitramines) (**2a—f**) (Scheme 1).

The efficiency of the condensation depends on the pH of the medium (the optimum value is 6.5—7.0) and the *N*-alkylsulfamate : formaldehyde ratio (the optimum ratio is 2—0.95). The reaction is reversible and proceeds through an intermediate hydroxymethyl derivative of *N*-alkylsulfamate. Methylenebissulfamates **1** are formed only upon complete removal of water, while their dissolution in water results in a mixture of the starting *N*-alkylsulfamates and their hydroxymethyl derivatives.

Scheme 1



1a—f **2a—f**

1: R = Me (**a**); Et (**b**); Bu^n (**c**); CH_2CH_2OH (**d**); $(CH_2)_3OH$ (**e**); $CH_2CH(OH)Me$ (**f**)
2: R' = Me (**a**); Et (**b**); Bu^n (**c**); $(CH_2)_2ONO_2$ (**d**); $(CH_2)_3ONO_2$ (**e**); $CH_2CH(ONO_2)Me$ (**f**)
M = K, Na

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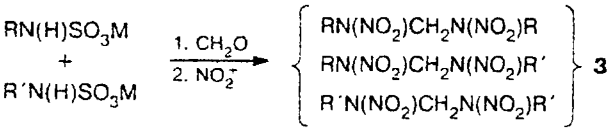
Sulfamates **1a—f** were nitrated with HNO_3—H_2SO_4 or HNO_3—Ac_2O mixtures.

As in the reaction of formaldehyde with two primary nitramines,[2] similar condensation of a mixture of two *N*-alkylsulfamates with formaldehyde and nitration of the resulting products afforded mixtures of three *N,N'*-dialkylmethylenebis(nitramines) **3** in 56—68% yield (Scheme 2). The composition of the mixtures was determined by GLC.[2] Thus, the nitration of the reaction product of potassium *N*-methyl- and *N*-ethylsulfamates with formaldehyde gives a ternary mixture **3a** (yield 68%): 2,4-dinitro-2,4-diazapentane, 2,4-dinitro-2,4-diazahexane, and 3,5-dinitro-3,5-diazaheptane.

Scheme 2



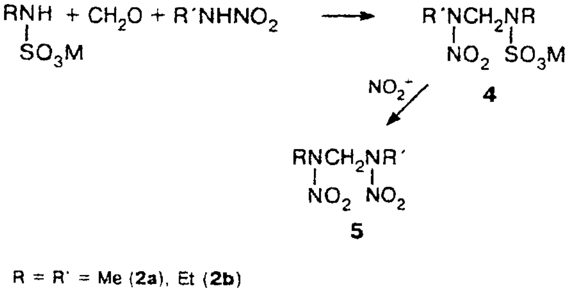
M = K, Na, NH_4

	3a	**3b**	**3c**
R	Me	Me	Et
R'	Et	Bu^n	Bu^n

Previously, ternary mixtures **3a—c** were obtained by condensation of mixtures of the corresponding nitramines with paraform.[2]

To identify and determine the physicochemical properties of the resulting mixtures, it was necessary to develop a convenient method for the preparation of unsymmetrical *N,N'*-dialkylmethylenebis(nitramines) ($RN(NO_2)CH_2N(NO_2)R'$, where $R \neq R'$). For this purpose, we carried out the reaction of *N*-alkylsulfamates with *N*-alkylnitramines and formaldehyde (Scheme 3).

Scheme 3



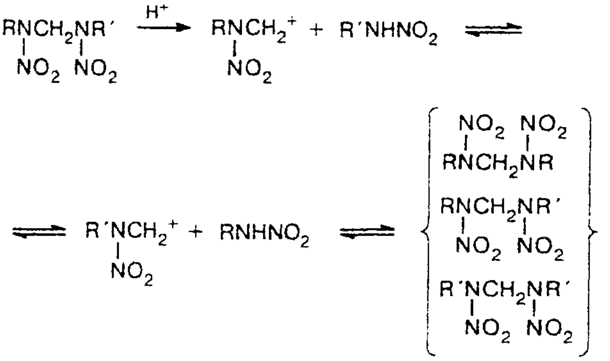
R = R' = Me (**2a**), Et (**2b**)

	5a	**5b**	**5c**	**5d**	**2a**	**2b**
R	Et	Bu^n	Pr	$(CH_2)_2ONO_2$	Me	Et
R'	Me	Me	Me	Me	Me	Et

To avoid the self-condensation of sulfamates, an excess of *N*-alkylnitramine was used, which was then removed from the reaction products **4** by extraction with ether.

The nitration of compounds **4** with HNO_3 in H_2SO_4 yields a mixture of three *N,N'*-dialkylmethylenebis(nitramines), which is probably due to disproportionation of *N,N'*-dialkylmethylene(bisnitramines) (Scheme 4).

Scheme 4



The disproportionation can be suppressed by using 98% HNO_3 at −20 to −30 °C or an HNO_3+Ac_2O mixture as the nitrating agents. The yields of compounds **5** were ~55—70%.

Experimental

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

2,4-Dinitro-2,4-diazapentane (2a). Potassium *N*-methylsulfamate (2.98 g, 20 mmol) and 30% formaldehyde (0.95 g) were added to 15 mL of 40% EtOH. The reaction mixture was concentrated on a rotary evaporator, and the resulting product **1a** (3.06 g, m.p. (decomp.) ~165—170 °C) was added with stirring at −10 °C to a mixture of 93% H_2SO_4 (5 mL) and 98% HNO_3 (6 mL). After 40 min, the reaction mixture was poured into a mixture of water (40 mL) with ice. The products were extracted with AcOEt (2×10 mL). The extract was successively washed with water (2×10 mL), 3% Na_2CO_3 (2×10 mL), and water (1×10 mL) and concentrated to give 2,4-dinitro-2,4-diazapentane (1.25 g, ~76%), m.p. 54 °C (EtOH) (*cf.* Ref. 1: m.p. 54 °C). Analogously, the following compounds were obtained: **2b**, yield 67%, m.p. 74—75 °C (*cf.* Ref. 1: m.p. 75 °C); **2c**, yield 64%, m.p. 88 °C (*cf.* Ref. 1: m.p. 88 °C); and **2d**, yield 68%, m.p. 93—95 °C (*cf.* Ref. 5: m.p. 94 °C). ^1H NMR, δ: 4.20 (t, 4 H, 2 CH_2N, *J* = 5.5 Hz); 4.88 (t, 4 H, 2 CH_2O, *J* = 5.0 Hz); 5.7 (s, 2 H, NCH_2N). **2e**, yield 70%, m.p. 88 °C. Found (%): C, 24.64; H, 4.09; N, 23.89. $C_7H_{14}N_6O_{10}$. Calculated (%): C, 24.57; H, 4.12; N, 24.56. ^1H NMR, δ: 1.95 (m, 4 H, 2 $CH_2C\underline{H}_2CH_2$); 4.15 (t, 4 H, 2 CH_2N, *J* = 6.0 Hz); 4.89 (t, 4 H, 2 CH_2O, *J* = 5.0 Hz); 5.65 (s, 2 H, NCH_2N). **2f**, yield 62%, m.p. 98 °C. Found (%): C, 24.89; H, 4.51; N, 24.11. $C_7H_{14}N_6O_{10}$. Calculated (%): C, 24.57; H, 4.12; N, 24.56. ^1H NMR, δ: 1.49 (m, 6 H, 2 Me); 4.1—4.45 (m, 4 H, 2 NCH_2); 5.58 (m, 2 H, 2 CH); 5.82 (m, 2 H, NCH_2N).

A ternary mixture (3a). Potassium *N*-methylsulfamate (2.98 g, 20 mmol), potassium *N*-ethylsulfamate (3.26 g, 20 mmol), and 30% formaldehyde (1.95 g) were added to

20 mL of 40% EtOH. The solvent was removed. The residue (6.20 g) was added to a mixture of 93% H_2SO_4 (10 mL) and 98% HNO_3 (12 mL) at −10 °C, and the reaction mixture was stirred at this temperature for 40 min and then poured into a water—ice mixture (80 mL). The products were extracted with CH_2Cl_2 (2×20 mL), and the extract was successively washed with water (2×15 mL), 3% Na_2CO_3 (2×15 mL), and water (1×15 mL) and concentrated to give **3a** (68%), m.p. 10—12 °C (*cf.* Ref. 2: m.p. 8—10 °C). Composition (mol %): $MeN(NO_2)CH_2N(NO_2)Me$ ~26, $MeN(NO_2)CH_2N(NO_2)Et$ ~50, and $EtN(NO_2)CH_2N(NO_2)Et$ ~24. Analogously, the following products were obtained: **3b**, yield 62%, m.p. 18—22 °C (*cf.* Ref. 2: m.p. 18—22 °C), $MeN(NO_2)CH_2N(NO_2)Me$ ~27%, $MeN(NO_2)CH_2N(NO_2)Bu^n$ ~50%, $Bu^nN(NO_2)CH_2N(NO_2)Bu^n$ ~23%; **3c**, yield 56%, m.p. 25—30 °C (*cf.* Ref. 2: m.p. 25—30 °C), $EtN(NO_2)CH_2N(NO_2)Et$ ~25%, $EtN(NO_2)CH_2N(NO_2)Bu^n$ ~51%, $Bu^nN(NO_2)CH_2N(NO_2)Bu^n$ ~24%.

2,4-Dinitro-2,4-diazahexane (5a). Potassium *N*-ethylsulfamate (1.64 g, 10 mmol), *N*-methylnitramine (0.91 g, 12 mmol), and 30% formaldehyde (0.95 g) were added to 10 mL of 40% EtOH. The reaction mixture was adjusted to pH ~4.6 and concentrated. The residue was washed with ether to give compound **4a** (2.47 g). This product was added to 8 mL of 98% HNO_3 at −20 to −25 °C. The resulting solution was stirred at this temperature for 1 h and then poured into 20 mL of a water—ice mixture. The products were extracted with AcOEt (2×10 mL). The extract was successively washed with water (2×10 mL), 3% Na_2CO_3 (2×10 mL), and water (1×10 mL) and concentrated to give compound **5a** (~67%), m.p. 32—33 °C (EtOH) (*cf.* Ref. 2: m.p. 31—32 °C). Analogously, the following compounds were obtained: **5b**, yield 56%, m.p. 35—36 °C (*cf.* Ref. 2: m.p. 36 °C); **5c**, yield 54%, m.p. 38 °C (*cf.* Ref. 2: m.p. 38 °C); **5d**, yield 58%, m.p. 54 °C. Found (%): C, 19.85; H, 4.00; N, 29.39. $C_4H_9N_5O_7$. Calculated (%): C, 20.09; H, 3.79; N, 29.28. ^1H NMR, δ: 3.50 (s, 3 H, MeN); 3.90—4.20 (t, 2 H, CH_2N, J = 5.5 Hz); 4.85 (t, 2 H, CH_2ONO_2, J = 5.0 Hz); 5.68 (s, 2 H, NCH_2N); **2a**, yield 72%, m.p. 54 °C (*cf.* Ref. 1: m.p. 54 °C); **2b**, yield 70%, m.p. 74—76 °C (*cf.* Ref. 1: m.p. 75 °C).

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