Sulfamic acid and *N*-alkylsulfamates in the synthesis of nitro derivatives of guanidine and aminofurazan

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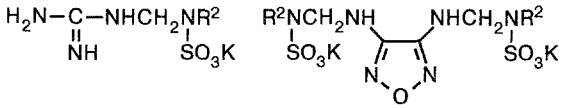
The *N*-nitro derivatives of the products of the condensation of formaldehyde with sulfamic acid derivatives and guanidine, nitroguanidine, 3,4-diaminofurazan, and 3-amino-4-methylfurazan have been synthesized.

Key words: guanidine, nitroguanidine; 3,4-diaminofurazan, 3-amino-4-methylfurazan; *N*-alkylsulfamates, sulfamic acid, *N*-nitration, nitramines.

Previously[1] we synthesized *N*-nitro derivatives of the products of the condensation of formaldehyde (**1**) with urea and primary *N*-alkylsulfamates (**2**).

In the present work we studied the possibility of applying this method to synthesizing *N*-nitro derivatives from guanidines and aminofurazans. The starting compounds were obtained by the condensation of formaldehyde and sulfamic acid derivatives **2a,b** with guanidinium chloride or nitrate (**3**), nitroguanidine (**4**), 3,4-diaminofurazan (**5**), and 3-amino-4-methylfurazan (**6**). All of these reactions gave colorless crystalline substances. We were unable to isolate pure condensation products, and they were characterized only as their *N*-nitro derivatives (**7**—**11**) (Scheme 1).

Based on the structures of the nitration products, it can be assumed that the condensation results in type **A** compounds (**12**, **13**) (see Scheme 1).



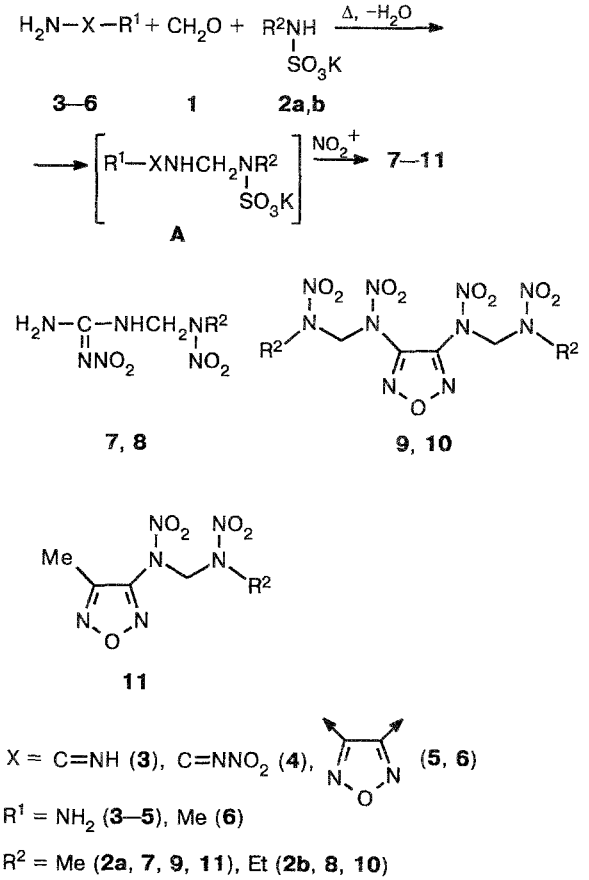
12a,b **13a,b**

12, **13**: R^2 = Me (**a**); Et (**b**)

Judging by the structures of nitro compounds **9** and **10**, diaminofurazan, unlike guanidine and urea,[1] reacts according to Scheme 1 with replacement of the hydrogen of both amino groups and the intermediate formation of sulfamate **13**. However, we believe that the reaction under consideration also involves the interme-

† Deceased.

Scheme 1



X = C=NH (**3**), C=NNO$_2$ (**4**), (**5**, **6**)

R^1 = NH_2 (**3**—**5**), Me (**6**)

R^2 = Me (**2a**, **7**, **9**, **11**), Et (**2b**, **8**, **10**)

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 4, pp. 719—721, April, 1995.

1066-5285/95/4404-0699 $12.50

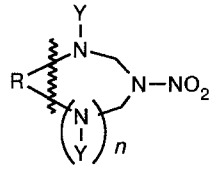
diate formation of the monosubstituted *N*-sulfo derivative of diaminofurazan, similar to structure **12** for guanidine.

Varying the reagent ratio and the pH of the medium used in the condensation did not give any other nitro derivatives of guanidine and furazan. In all cases, the optimum pH was 5.0—6.5. The yields of nitramines **9** and **10** increased when the excess of the starting compounds **1** and **2** was increased (Table 1).

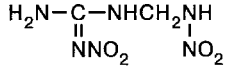
When nitroguanidine **4** was used instead of guanidine, only a small yield of nitramine **7** according to Scheme 1 was obtained due to the low solubility of compound **4** in water and ethanol, which were used as solvents in the condensation. As a result, nitroguanidine **4** partially precipitated during condensation, and up to 10 % of the starting amount of **4** remained unreacted and precipitated along with compound **7** during the nitration stage. The condensation of **4** with potassium *N*-methylsulfamate and formaldehyde without a solvent at 70—120 °C did not give **7** in a yield above 20 % either.

Taking into account the difference in the stability of the guanidine and furazan derivatives in the nitrating mixture, we chose the following nitration conditions:[2—7] HNO_3/oleum in the syntheses of **7** and **8** and HNO_3/H_2SO_4 in the syntheses of **9**—**11**.

We have found previously[8] that the synthesis of nitramines according to Scheme 1 from potassium sulfamate **2c** (R^2 = H) gives compounds **14** based on urea (**14a**), 3,4-diaminofurazan (**14b**), guanidine (**14c**), and 5-aminotetrazole (**14d**).



14a—d



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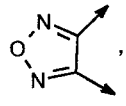
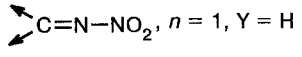
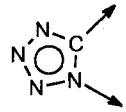
14a: R = C=O, *n* = 1, Y = NO_2

14b: R =  , *n* = 1, Y = NO_2

14c: R =  , *n* = 1, Y = H

14d: R =  , *n* = 0, Y = NO_2

A more thorough study of the condensation of guanidine with potassium sulfamate and formaldehyde showed that the nitration products contain a linear nitramine (**15**) in addition to the cyclic compound **14c**. When the molar ratio of the starting condensation components is **3** : **1** : **2c** = 1 : 1 : 1, the primary nitramine **15** becomes the predominant reaction product (after nitration), and the yields of compounds **15** and **14c** are 25 and 5 %, respectively.

Table 1. Conditions of the synthesis of nitramines **7**—**11**

Starting compounds and their molar ratios at the condensation stage	pH	Nitration product	Yield (%)
3 : **1** : **2a** = 1 : 1 : 1	6.5	**7**	28
3 : **1** : **2b** = 1 : 1 : 1	6.5	**8**	30
4 : **1** : **2a** = 1 : 2 : 2	6.0	**7**	16
5 : **1** : **2a** = 1 : 2 : 2	5.0	**9**	11
5 : **1** : **2a** = 1 : 6 : 6	5.0	**9**	57
5 : **1** : **2b** = 1 : 2 : 2	6.0	**10**	7
5 : **1** : **2b** = 1 : 3 : 2	6.0	**10**	24
5 : **1** : **2b** = 1 : 6 : 4	6.0	**10**	20
6 : **1** : **2a** = 1 : 1 : 1	6.0	**11**	40

Experimental

^{1}H NMR spectra were recorded in acetone-d_6 on Bruker AM-300 (300 MHz) and Tesla BS-467 (60 MHz) spectrometers using HMDS as the internal standard. IR spectra were obtained in KBr pellets on a UR-20 spectrophotometer. The elemental analyses of the compounds synthesized agree with the calculated values.

***N*-(2-Nitro-2-azapropyl)-*N'*-nitroguanidine (7).** Guanidinium nitrate (1.22 g, 10 mmol) and 32 % formaldehyde (0.9 mL, 10 mmol) were added to a solution of potassium *N*-methylsulfamate (1.49 g, 10 mmol) in water (5 mL), the pH was adjusted to 6.5, and the mixture was concentrated on a rotary evaporator at bath temperature of 100—110 °C. The resulting crystalline precipitate (2.8 g) was added at 0 °C to a mixture of 25 % oleum (8 mL) and 97 % HNO_3 (4 mL). The reaction mixture was stirred for 1 h at 0—10 °C, poured onto ice (30 g), and extracted with ethyl acetate (5 × 20 mL). The extract was washed with water (2 × 20 mL), 3 % aqueous sodium carbonate (20 mL), and water (20 mL) and concentrated *in vacuo*. The residue was recrystallized from an ethanol—acetone mixture (6 : 1), yield 28 %, m.p. 168—170 °C. IR, ν/cm^{-1}: 3410, 3300, 1620, 1590, 1515, 1300. ^{1}H NMR, δ: 3.5 (s, 3 H, Me); 5.63 (s, 2 H, CH_2). The product was identified by comparison with an authentic sample obtained previously by O. A. Luk'yanov and T. G. Mel'nikova (Institute of Organic Chemistry, RAS) using a different procedure.

***N*-(2-Nitro-2-azabutyl)-*N'*-nitroguanidine (8)** was obtained similarly to compound **7** using potassium *N*-ethylsulfamate (10 mmol) instead of potassium *N*-methylsulfamate, yield 30 %, m.p. 156—158 °C. IR, ν/cm^{-1}: 3420, 3310, 3250, 1625, 1550, 1515, 1425, 1290. ^{1}H NMR, δ: 1.13 (t, 3 H, Me); 3.24 (q, 2 H, CH_2—C); 5.32 (s, 2 H, NCH_2N).

Bis(1,3-dinitro-1,3-diazabutyl)furazan (9). A solution of formaldehyde (30 %, 2.7 g) was added to a solution of compound **2a** (4.47 g, 30 mmol) and compound **5** (0.5 g, 5 mmol) in water (20 mL), and the pH of the medium was adjusted to 5.0 by adding 5 % aqueous KOH. The solution was concentrated on a rotary evaporator at 80—100 °C until a crystalline precipitate was formed. A mixture of these crystals (2.7 g) and methylamine hydrochloride (0.3 g) was added at −20 °C to a mixture of HNO_3 (d = 1.5 g cm^{-3}, 8 mL) and Ac_2O (8 mL), and the reaction mixture was stirred for 1 h at 0—5 °C and

poured onto ice (100 g). The resulting sticky precipitate was dissolved in ethyl acetate (70 mL) and washed with water (30 mL), 3 % $NaHCO_3$ (until the washing water became slightly alkaline), and water (30 mL), dried with $MgSO_4$, and concentrated. Ether (40 mL) was added to the precipitate, and the mixture was left overnight. The ether was decanted, and the precipitate was dissolved in a minimum amount of acetone. After precipitation of the first crystals, ether (20 volume parts) was added to the acetone. Yield 55 %, m.p. 144 °C (dec.). ^1H NMR, δ: 3.5 (s, 3 H, Me); 6.18 (s, 2 H, CH_2). The product was identified by comparison with an authentic sample obtained previously by I. V. Tselinskii *et al.* (Institute of Technology, Saint Petersburg) using a different procedure.

Bis(1,3-dinitro-1,3-diazapentyl)furazan (10) was obtained similarly to compound **9** using potassium *N*-ethylsulfamate (30 mmol). The molar ratio of the components was **5** : **1** : **2b** = : 3 : 2, pH = 6.0. Yield 24 %, m.p. 144 °C (dec.). IR, ν/cm^{-1}: 1000, 1080, 1280, 1400, 1520, 1580. ^1H NMR, δ: 1.17 (t, 3 H, Me); 3.97 (q, 2 H, CH_2—C); 6.2 (s, 2 H, CH_2N).

3-(1,3-Dinitro1,3-diazapropyl)-4-methylfurazan (11) was obtained similarly to compound **9** at the molar ratio of the components **6** : **1** : **2a** = 1 : 1 : 1, pH = 6.0. Yield 40 %, m.p. 140—142 °C (dec.). IR, ν/cm^{-1}: 907, 1095, 1290, 1590, 3035. ^1H NMR, δ: 2.2 (s, 3 H, Me—C); 3.5 (s, 3 H, Me—N); 5.9 (s, 2 H, CH_2).

***N*-(2-Nitro-2-azaethyl)-*N'*-nitroguanidine (15).** Guanidinium nitrate (1.22 g, 10 mmol) and 32 % formaldehyde (0.9 g, 10 mmol) were added to a solution of potassium sulfamate (1.35 g, 10 mmol) in water (5 mL). The solution pH was adjusted to 6.5, and the mixture was concentrated *in vacuo* at 110—120 °C until crystals (2.7 g) were obtained. The latter were added at 0 °C to a mixture of 96 % H_2SO_4 (8 mL) and 97 % HNO_3 (4 mL). The mixture was stirred for 1 h at 10 °C, poured onto ice (30 g), and extracted with ethyl acetate (5 × 20 mL). The extract was washed with water (3 × 20 mL) and concentrated. The residue was recrystallized from an ethanol—acetone mixture (6 : 1). The resulting crystals of compound **14c** were filtered off, yield 5 %, m.p. 215—216 °C (*cf.* Ref. 8: m.p. 215—216 °C). The mother liquor was concentrated on a rotary evaporator, and the residue was recrystallized from ether. The yield of **15** was 24 %, m.p. 144 °C. IR, ν/cm^{-1}: 3380, 3140, 1655, 1560—1600, 1430, 1295—1315. ^1H NMR, δ: 5.38 (s, CH_2).

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Received September 9, 1994