Sulfonyldiazene-*N*-oxides

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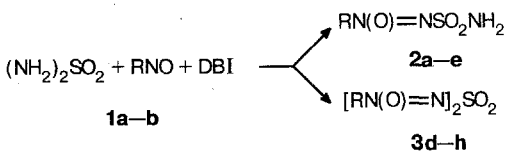
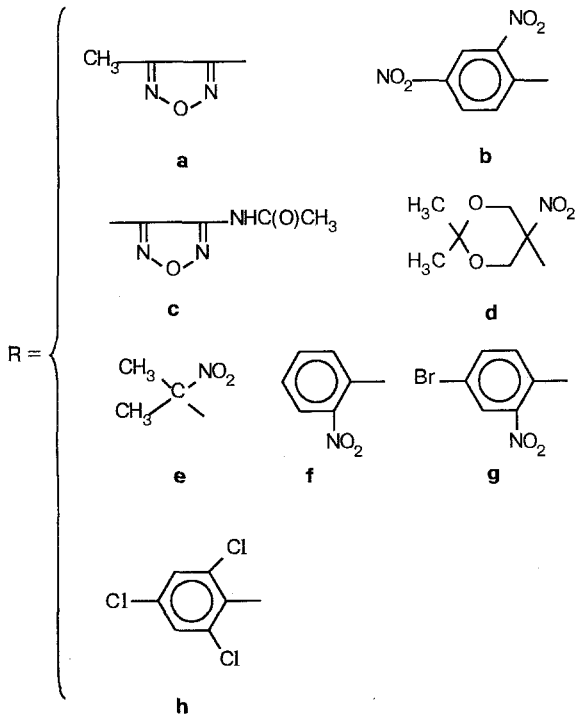
Sulfonyldiazene-*N*-oxides **2** and **3** were obtained by treatment of sulfamide with nitroso compounds **1** in the presence of 1,3-dibromoisocyanurate (DBI) in neutral and acid media.

Key words: nitroso compounds, oximes, diazene-*N*-oxides, sulfamide, 1,3-dibromoisocyanurate.

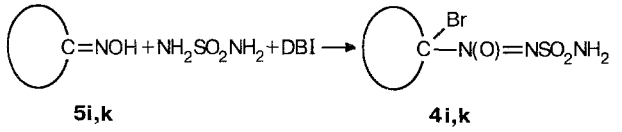
The method for the synthesis of sulfonyldiazene-*N*-oxides (SDO's) of the general formula $ArSO_2N{=}N(O)R$ by treatment of *N,N*-dihaloarenesulfamides with nitroso compounds is known.[1] However, this reaction is not suitable in the case of sulfamide, because its *N,N*-dihalo-derivatives are unstable and cannot be isolated. We found that SDO's are formed in a reaction of nitroso compounds **1** with sulfamide in the presence of DBI (*cf.* Ref. 2).





As a rule, the reaction results in a mixture of SDO's **2** and **3**. The relative rates of their formation depend on the substituent R. For example, only **2a—c** can be obtained from **1a—c**, whereas only **3f—h** are formed from **1f—h**. In the case of compound **1d**, the reaction mixture contains SDO's **2d** and **3d**. The formation of compounds **2** and **3** is accelerated several times in the presence of acids, such as HBr, $MeCO_2H$, CF_3CO_2H, HCl, or H_2SO_4. HBr acts most efficiently: SDO's **2c,e** could be obtained in the presence of this acid. They could not be isolated without the acid, although TLC detected them after the reaction mixture was kept for several days. Compound **2d** can be obtained from **1a** in the presence of HBr. Compounds **3a—c** could not be obtained from **2a—c** even in the presence of acids.

SDO's **4i,k** can also be obtained by the reaction of sulfamide and DBI with some oximes of cyclic ketones, such as cyclohexanone (**5i**) and adamantanone (**5k**).



i = cyclohexyl, **k** = adamantyl

SDO's **4** are only formed in the presence of acids. No products of type **3** could be detected. This method did not allow us to transform acetoxime into the corresponding SDO.

Experimental

Compound **1c** was kindly provided by A. B. Sheremet'ev (Institute of Organic Chemistry, RAS).

Synthesis of 1-(4-methylfurazanyl)-2-aminosulfonyldiazene-1-oxide (2a) and 1-(2,4-dinitrophenyl)-2-aminosulfonyldiazene-1-oxide (2b). DBI (a 10 % excess with respect to the sulfamide) was added at 10—12 °C to a solution of equimolar amounts of

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 4, pp. 681—683, April, 1994.

1066-5285/94/4304-0632 $12.50

compound **1a** or **1b**[3,4] and sulfamide (a 10—15 % excess) in dry dioxane. The reaction mixture was stirred for 5—6 h and kept for 12 h at 20 °C. The precipitate was filtered off, the filtrate was concentrated, and the residue was chromatographed on a column with silica gel L40/100 (gradient elution: chloroform, ethyl acetate for **2a**, benzene, chloroform for **2b**). Compound **2a**, yield 43.5 %, m.p. 96 °C (from chloroform). Found (%): C, 17.51; H, 2.21; N, 33.68; S, 15.26. $C_3H_5N_5O_4S$. Calculated (%): C, 17.39; H, 2.42; N, 33.82; S, 15.46. IR (KBr), ν/cm^{-1}: 1190 (SO_2); 1300, 1480 ((N(O)=N); 3220, 3370 (NH_2). ^{1}H NMR ($(CD_3)_2CO$), δ: 2.60 (s, 3H, Me), 7.3 (br.s, NH_2). **2b**, yield 67 %, m.p. 152 °C (from benzene). Found (%): C, 24.37; H, 1,72; N, 23.78; S, 10.64. $C_6H_5N_5O_7S$. Calculated (%): C, 24.70; H, 1.70; N, 24.05; S, 11.00. IR (KBr), ν/cm^{-1}: 1180 (SO_2); 3240, 3360 (NH_2).

Synthesis of 1-(4-acetylaminofurazanyl)-2-aminosulfonyldiazene-1-oxide (2c). DBI (4 g, 14 mmol) and HBr (0.52 g, 6.4 mmol) were successively added at 10 °C to a solution of compound **1c** (1 g, 6.4 mmol) and sulfamide (0.65 g, 6.8 mmol) in dry dioxane. The temperature was increased to 25 °C. The reaction mixture was stirred for 3 h, concentrated to dryness, and extracted with ether. The extract was concentrated, and the residue was chromatographed on a column with silica gel L40/100 (chloroform as the eluent) to give 1.1 g (68.8 %) of compound **2C**, m.p. 139—140 °C (dec.). Found (%): C, 19.31; H, 2.27; N, 33.41; S, 12.90. $C_4H_6N_6O_5S$. Calculated (%): C, 19.20; H, 2.42; N, 33.59; S, 12.81. IR (KBr), ν/cm^{-1}: 1180 (SO_2); 1310, 1480 [N(O)=N]; 1680 (CO); 3270, 3380 (NH_2).

Synthesis of 1-(2,2-dimethyl-5-nitro-1,3-dioxanyl-5)-2-aminosulfonyldiazene-1-oxide (2d). HBr (0.6 mmol) in dioxane and DBI (1.5 g, 5.2 mmol) were successively added at 10 °C to a solution of compound **1d** [5] (0.4 g, 2.1 mmol) in dry dioxane (10 mL). The mixture was stirred for 10 min, then the temperature was increased to 20 °C, and a solution of sulfamide (0.22 g, 2.3 mmol) in dioxane (7 mL) was added dropwise. The mixture was stirred for 1 h until compound **1d** disappeared completely (TLC monitoring). The precipitate that formed was filtered off and washed with dioxane and benzene. The filtrate was concentrated, benzene (5 mL) was added, and the mixture was poured into water (10 mL). Aqueous NaOH was added to pH 10, the benzene layer was separated, and the aqueous layer was washed with benzene (2×4 mL). The aqueous layer was acidified with CF_3COOH to pH 4 and extracted with ethyl acetate. The extract was dried with Na_2SO_4, the solvent was distilled off, and the residue was chromatographed on a column with silica gel L40/100 ($CHCl_3$: CH_3OH, 25 : 1 as the eluent) to give 0.4 g (70 %) of compound **2d**, m.p. 118 °C. Found (%): C, 25.54; H, 4.07; N, 19.61; S, 11.12. $C_6H_{12}N_4O_7S$. Calculated (%): C, 25.35; H, 4.26; N, 19.71; S, 11.28. IR (KBr), ν/cm^{-1}: 1180 (SO_2); 1280, 1480 [N(O)=N]; 1370, 1580 (NO_2); 3240, 3410 (NH_2). ^{1}H NMR ($(CD_3)_2CO$), δ: 1.41 (s, 3H, Me), 1.43 (s, 3H, Me), 4.75 (s, 4H, CH_2), 7.47 (br., 2H, NH_2).

Synthesis of 1-(2-nitropropyl)-2-aminosulfonyldiazene-1-oxide (2e). SDO **2e** was obtained similarly to compound **2d** (reaction time 24 h). Ether was used for the extraction. Chromatographic purification was not carried out. The yield of product **2e** was 64.5 %, m.p. 90 °C (from chloroform). IR (KBr), ν/cm^{-1}: 1190 (SO_2); 1350, 1480 [N(O)=N]; 1380, 1570 (NO_2); 3300, 3390 (NH_2). ^{1}H NMR ($(CD_3)_2CO$), δ: 1.71 (s, 6H, Me); 4.47 (br.s, 2H, NH_2).

Synthesis of 2,2-sulfonyl-bis-1-(2,2-dimethyl-5-nitro-1,3-dioxanyl-5)diazene-1-oxide (3d). DBI (0.6 g, 2.1 mmol) was added at 20 °C to a solution of compounds **2d** (0.5 g, 1.8 mmol) and **1d** (0.34 g, 1.8 mmol) in a mixture of MeCN (20 mL) and dioxane (5 mL). The mixture was stirred for 1.5 h at this temperature and for 2 h at 35 °C, then Na_2HPO_4 (10 g) was added. The mixture was stirred for 30 min and evaporated to dryness. The residue was extracted with benzene, the extract was concentrated to a volume of 5 mL, and a solution of ammonia in ethanol was added to pH 8—9. The solution was evaporated to dryness, and ether (50 mL) was added. The mixture was repeatedly washed with aqueous $NaHCO_3$ and dried with $MgSO_4$. The ether was distilled off, and the remaining oil was chromatographed on a column with silica gel L40/100 ($CHCl_3$ as the eluent) to give 0.6 g of compound **3d** (70.6 %) as an oil. Found (%): C, 30.72; H, 4.08; N, 17.51; S, 6.55. $C_{12}H_{20}N_6O_{12}S$. Calculated (%): C, 30.51; H, 4.27; N, 17.79; S, 6.79. IR (KBr), ν/cm^{-1}: 1180 (SO_2); 1280, 1500 [N(O)=N]; 1380, 1580 (NO_2). ^{1}H NMR ($(CD_3)_2CO$), δ: 1.40 (s, 6H, Me), 1.43 (s, 6H, CH_3), 4.78 (s, 8H, CH_2).

Synthesis of 2,2-sulfonyl-bis-1-(2-nitropropyl-2)diazene-1-oxide (3e). HBr (0.05 g, 6 mmol), DBI (3.6 g, 12 mmol), and compound **2e** (0.13 g, 5.9 mmol) were successively added at 10 °C to a solution of compound **1e** [6] (0.7 g, 5.9 mmol) in dioxane. The mixture was stirred for 15 h at 20 °C, concentrated, and the residue was extracted with ether. The extract was concentrated, and the residue was chromatographed on a column with silica gel L40/100 ($CHCl_3$ as the eluent) to give 0.6 g (30 %) of compound **3e**, m.p. 89 °C. Found (%): C, 21.72; H, 3.50; N, 25,44; S, 9.61. $C_6H_{12}N_6O_8S$. Calculated (%): C, 21.95; H, 3.68; N, 25.60; S, 9.77. IR (KBr), ν/cm^{-1}: 1180 (SO_2); 1320, 1370, 1390 [NO_2, N(O)=N]; 1500 [N(O)=N]; 1580 (NO_2). ^{1}H NMR ($(CD_3)_2CO$), δ: 1.73 (s, Me).

Synthesis of 2,2-sulfonyl-bis-1-(2-nitrophenyl)- (3f), 2,2-sulfonyl-bis-(4-bromo-2-nitrophenyl)- (3g), and 2,2-sulfonyl-bis-1-(2,4,6-trichlorophenyl)diazene-1-oxide (3h). A solution of compound **1f—h** [7,8,9] (2 mmol), sulfamide (3 mmol), and DBI (4.4 mmol) in dry dioxane (15 mL) was stirred at 20 °C until compound **1f—h** disappeared (TLC monitoring), then the precipitate was filtered off. The product was purified by recrystallization or by chromatography on a column (silica gel L40/100, chloroform as the eluent). Compound **3f**, reaction time 1 day, purification by chromatography, yield 34 %, m.p. 154 °C. Found (%): C, 36.60; H, 2.17; N, 21.11; S, 7.93. $C_{12}H_8N_6O_8S$. Calculated (%): C, 36.37; H, 2.03; N, 21.21; S, 8.09. IR (KBr), ν/cm^{-1}: 1180 (SO_2); 1320, 1480 [N(O)=N]; 1360, 1530 (NO_2). Compound **3g**, reaction time 4 days, purification by chromatography, yield 77 %, m.p. 174 °C (reprecipitation with ether from ethanol). Found (%): C, 26.25; H, 1.27; Br, 28.89; N, 14.87; S 5.68. $C_{12}H_6Br_2N_6O_8S$. Calculated (%): C, 26.01; H, 1.09; Br, 28.84; N, 15.17; S, 5.79. IR (KBr), ν/cm^{-1}: 1180 (SO_2); 1320, 1460 [N(O)=N], 1370, 1520 (NO_2). Compound **3h**, reaction time 1 day, purification by recrystallization, yield 61 %, m.p. 230—232 °C (CH_3OH : C_6H_6, 1 : 2). Found (%): C, 28.36; H, 1.22; Cl, 41.57; N, 10.88; S, 6.26. $C_{12}H_4Cl_6N_4O_4S$. Calculated (%): C, 28.10; H, 0.79; Cl, 41.47; N, 10.92; S, 6.25. IR (KBr), ν/cm^{-1}: 1170 (SO_2), 1310, 1460 [N(O)=N].

If HBr is present, the yields of compounds **3f—h** do not change, but the reaction times decrease to two—three hours.

Synthesis of 1-(1-bromocyclohexyl)-2-aminosulfonyldiazene-1-oxide (4i) and 1-(2-bromoadamantyl-2)-2-aminosulfonyldiazene-1-oxide (4k). HBr (5.4 mmol) in dioxane and DBI (11 mmol) were added successively at 3 °C to a solution of compound **5i,k** (5.4 mmol) and sulfamide (5.4 mmol) in a mixture of dioxane (30 mL) and dry MeCN (10 mL). The temperature was increased to 20 °C, and the mixture was

stirred for 3 h. The solvent was distilled off, the residue was extracted with ether, the ether was distilled off, and the residue was chromatographed on a column (silica gel L40/100, eluent: ether for **4i**, benzene for **4k**). SDO **4i**, yield 41.5 %, m.p. 92—93 °C (from 50 % aqueous methanol). Found (%): C, 25.06; H, 4.18; Br, 27.66; N, 14.80; S, 10.96. $C_6H_{12}BrN_3O_3S$. Calculated (%): C, 25.19; H, 4.23; Br, 27.92; N, 14.68; S, 11.20. IR (KBr), ν/cm^{-1}: 1180 (SO_2); 1360, 1490 [N(O)=N]; 3310, 3410 (NH_2). SDO **4k**, yield 42.5 %, m.p. 157 °C. Found (%): C, 35.54; H, 4.08; Br, 23,85 N, 12.54 S, 9.44. $C_{10}H_{14}BrN_3O_3S$. Calculated (%) (%): C, 35.73; H, 4.20; Br, 23.77; N, 12.50; S, 9.54. IR (KBr), ν/cm^{-1}: 1180 (SO_2); 1370, 1480 [N(O)=N]; 3270, 3380, (NH_2).

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Received November 21, 1993