Reaction of Nitrile Oxides with N_2O_3 (general method). To a solution of 5 mmoles of the nitrile oxide in 15 ml of abs. CH_2Cl_2 is added at 20°C a solution of 5 mmoles of N_2O_3, prepared according to [6], in 1 ml of CH_2Cl_2. The mixture was allowed to stand for 3 h, the nitrogen oxide and the solvent are evaporated, and the residue is worked up as described above.

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SULFYLIMINOFUROXANS: SYNTHESIS, STRUCTURE, AND OXIDATION TO NITRO AND NITROSO DERIVATIVES

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We have synthesized sulfylimines of the furoxan series. It was shown that by oxidation of 4-dimethylsulfyliminofuroxans both nitro and nitroso derivatives, the first examples of nitrosofuroxans, can be prepared. With x-ray structural analysis the main structural characteristics of the sulfyliminofuroxans were established.

In recent years the interest in methods to synthesize and to chemically convert aromatic and heterocyclic sulfylimines has grown considerably. Sulfylimines of the pyridine [1-3], pyrimidine [1, 4, 5], pyrazine [5-7], and furazan [8] series and of other heterocyclic compounds have been studied. Yet sulfyliminofuroxans have not been described.

The purpose of this work was to study the possibility of synthesizing 3- and 4-dimethylsulfyliminofuroxans, their structural characteristics, and their behavior in oxidation reactions.

For the synthesis of sulfyliminofuroxans we have investigated the reaction of aminofuroxans with the bis-triflate (I) and bis-trifluoroacetate (II) of dimethyl sulfide, which

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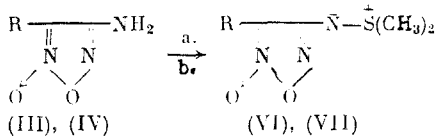
were used earlier for the synthesis of aromatic and heterocyclic sulfylimines [5-9]. As examples we selected 4-amino-3-phenyl- (III), 4-amino-3-methyl- (IV), and 3-amino-4-phenylfuroxan (V).

It was shown that 4-aminofuroxans (III) and (IV) give sulfylimino derivatives on reaction with (I) or (II).

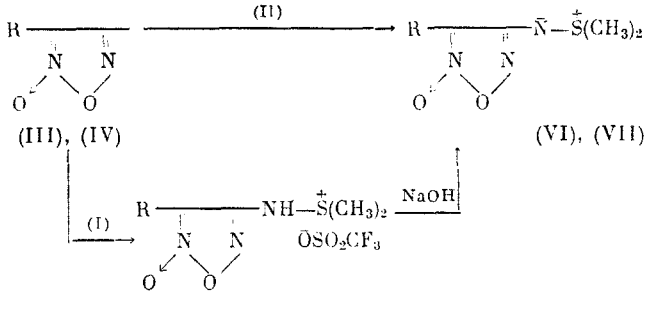


(III), (IV) (VI), (VII)

a. $(CH_3)_2\overset{+}{S}OSO_2CF_3\bar{O}SO_2CF_3$ (I); b. $(CH_3)_2\overset{+}{S}OCOCF_3\bar{O}COCF_3$ (II); R = Ph (III), (VI); Me (IV), (VII). Yield, %: (VI), 100 (a), 57 (b), (VII), 100 (a), 55 (b).

The yield of final products is significantly influenced by the amount of sulfylating agent: optimal is its 2.2-fold molar excess. That fact was unexpected because usually one mole of the agent is used [5-9]. We explain the involvement of the second mole in the reaction by possible coordination of the electrophilic sulfylating agent with the N-oxide oxygen atom of the furoxan ring.

The yields of sulfyliminofuroxans are considerably lower when using (II) than when using (I). To elucidate the nature of this phenomenon we have studied the course of the reaction between the aminofuroxan and the sulfylating agent. It was found that in the case of (I) the reaction stops at the stage of formation of the triflate salt of the sulfylimine and that for the preparation of the free sulfylimine it is necessary to work up the reaction mixture with an aqueous solution of a base. When (II) is used the stage of formation of the corresponding salt was not established (TLC data).



(III), (IV) (VI), (VII)

We have found that (I) and (II) gradually decompose authentic sulfylimines (VI) and (VII). Thus, the lowering of the yields of (VI) and (VII) in the case of reaction of the aminofuroxan with (II) results from the fact that reagent (II), which participates in the reaction, reacts with the sulfylimine; in the case of the same reaction with (I) this does not take place because the reaction stops at the stage of obtaining the sulfylimine salt, which is stable to the action of the sulfylating agent.

From the reactions of (I) and (II) with 3-amino-4-phenylfuroxan (V) we failed to isolate the sulfylimine. By means of TLC we noted the disappearance of the starting amine and the formation of a product that according to TLC data could correspond with the sulfylimine, but it decomposed when attempts to isolate it were made.

To elucidate the structural characteristics of the sulfyliminofuroxans we have carried out x-ray structural analysis of (VI). Figure 1 shows the general shape of the molecule and the bond lengths. The phenyl ring is rotated by 30° around the C^1–C^3 bond relative to the furoxan ring, which is also characteristic of other phenylfuroxans [10].

The ylide fragment of the dimethylsulfylimino group of (VI) is in cis-position with the endocyclic C=N bond and practically located in the plane of the furoxan ring: the torsion angles S–N^3–C^2–N^2 and S–N^3–C^1–C^2 are 7.0 and −174.1°, respectively. One of the methyl groups is somewhat flattened relative to that plane (the torsion angle C^9–S–N^3–C^2 is 165.5°), the other relative to the orthogonal (the torsion angle C^{10}–S–N^3–C^2 is 90°). The sulfur atom in the structure of (VI) has a pyramidal structure with valence angles N^3–S–C^9 100.24(9)° and C^9–S–C^{10} 110.11(1)°, and a somewhat larger value for the angle N^3–S–C^{10} [105.12(9)°].

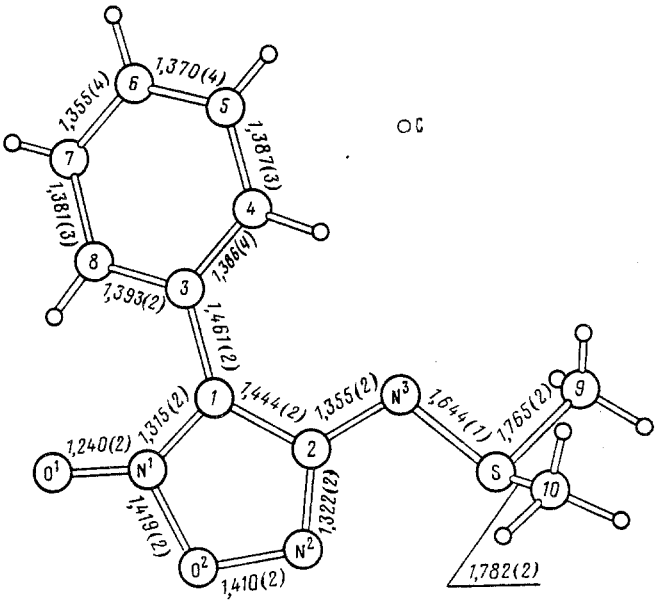


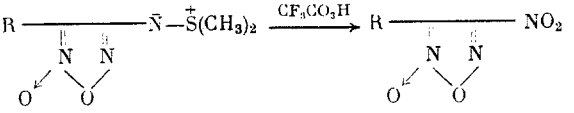
Fig. 1. Structure of molecule (VI) according to x-ray data. Bond lengths are in Å.

Introduction of a dimethylsulfylimino group at the furoxan ring changes the bond lengths of the furoxan significantly. Lengthening of the bonds C^1-C^2 [1.444(2) Å] and C^2-N^2 [1.322 (2) Å], and especially N^2-O^2 [1.410(2) Å] in comparison with the average values for the furoxan ring, which are 1.422, 1.304, and 1.380 Å, respectively. Thus, the bond lengths of the fragment $C^2=N^2-O^2$, adjacent to the dimethylsulfylimino group, are approximately lengthened to the same extent as in the case of addition of an oxygen atom to the nitrogen atom of that fragment in the furoxan ring. It is not to be excluded that this may lead to unusual chemical properties of the furoxan ring.

On the other hand, the bond N^1-O^2 [1.419(2) Å] at the N-oxide side of the ring is shortened in comparison with the average value (1.438 Å).

All these changes lead to mutual leveling of the C=N bonds and the N–O bonds of the furoxan ring. Analogous examples are not described in the literature.

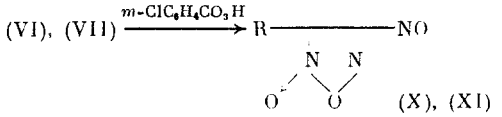
It is known that sulfylimines of heterocyclic compounds can be oxidized to either nitroso [1, 4, 11, 12] or nitro derivatives [8]. We have shown for the first time that depending on the oxidant sulfyliminofuroxans can give both nitro and nitroso compounds. Thus, the reactions of (VI) and (VII) with trifluoroperacetic acid lead to the 4-nitrofuroxans.



(VI), (VII) (VIII), IX)

R = Ph (VI), (VIII), Me (VII), (IX). Yield, %: 70 (VIII), 84 (IX).

On oxidation of sulfyliminofuroxans with m-chloroperbenzoic acid the first members of nitrosofuroxans were obtained: 4-nitroso-3-phenyl- and 4-nitroso-3-methylfuroxan.



(X), (XI)

R = Ph (X), Me (XI). Yield, %: 93 (X), 67 (XI).

Nitrosofuroxans are green compounds that do not form dimers of nitroso compounds even at −10°C.

EXPERIMENTAL

IR spectra were taken from KBr disks on a Specord spectrometer, UV spectra on a Specord UV-VIS spectrometer in CH_2Cl_2, PMR spectra on a Tesla BS-467 spectrometer (60 MHz, relative to TMS), and mass spectra on a Varian CH-6 instrument. ^{13}C and ^{14}N NMR spectra were recorded on a Bruker AM-300 spectrometer operating at 75.6 and 21.6 MHz relative to the internal standard TMS and the external standard nitric acid, respectively. TLC was carried out on Silufol UV-254 plates in the system chloroform–acetone 5:1.

4-Amino-3-phenyl- and 3-Amino-4-phenylfuroxan were prepared according to [13] and 4-Amino-3-methylfuroxan according to [14].

4-Dimethylsulfylimino-3-phenylfuroxan (VI). Method A. To a solution of 0.57 ml (8 mmoles) of DMSO in 5 ml of abs. CH_2Cl_2 is added at −60°C a solution of 2.06 g (7.3 mmoles) of $(CF_3SO_2)_2O$ in 8 ml of abs. CH_2Cl_2 while keeping the temperature below −55°C. The mixture was stored for 30 min and then a solution of 0.58 g (3.3 mmoles) of (III) in a mixture of 3 ml of DMSO and 5 ml of abs. CH_2Cl_2 was added dropwise. The reaction mixture was kept at −60°C for 30 min, then to it was added at −30°C and with vigorous stirring 8 ml of a 10% aqueous NaOH solution, and the temperature of the reaction mixture was gradually increased to 0°C. The organic layer was separated off and the aqueous layer was extracted with CH_2Cl_2 (2 × 3 ml). The combined organic extracts were extracted with 3 ml of water, dried over $MgSO_4$, and evaporated. Yield 0.78 g (100%) of (VI), mp 112°C, R_f 0.25. Found, %: C 50.63, H 4.68, N 16.83, S 13.42. $C_{10}H_{11}N_3O_2S$. Calculated, %: C 50.63, H 4.64, N 16.64, S 13.50. IR spectrum (ν, cm^{-1}): 3000, 2910 (CH_3), 970 ($>\overset{+}{S}-\overset{-}{N}-$). PMR spectrum (δ, ppm, CD_3CN): 2.85 s (CH_3), 7.38 and 8.45 m (Ph). Mass spectrum, m/z: 237 (M^+), 207, 177, 77.

In the same way was obtained 0.58 g (100%) of (VII), mp 105°C (dec.), R_f 0.26. Found, %: C 33.72, H 5.09, N 24.20, S 18.19. $C_5H_9N_3O_2S$. Calculated, %: C 34.29, H 5.14, N 24.00, S 18.29. IR spectrum (ν, cm^{-1}): 3020, 2910 (CH_3), 870 ($>\overset{+}{S}-\overset{-}{N}-$). PMR spectrum [δ, ppm, $(CD_3)_2CO$]: 1.85 s (CH_3 furox.), 2.85 s [$S(CH_3)_2$]. Mass spectrum, m/z: 175 (M^+):, 145, 105.

Method B. To a solution of 0.44 ml (6.2 mmoles) of DMSO in 2 ml of abs. CH_2Cl_2 is added at −60°C 0.70 ml (5 mmoles) of $(CF_3CO)_2O$ in such a way that the temperature of the reaction mixture does not exceed −50°C. After 15 min to the viscous white mass formed is added a solution of 0.39 g (2.2 mmoles) of (III) in a mixture of 1 ml of DMSO and 2 ml of abs. CH_2Cl_2. The reaction mixture is kept at −60°C for 2.5 h and then worked up as in Method A. Yield 0.30 g (57%) of (VI), mp 112°C.

In the same way was obtained 0.21 g (55%) of (VII), mp 105°C.

4-Nitro-3-phenylfuroxan (VIII). To a solution of 0.35 ml (12 mmoles) of 83% hydrogen peroxide in 10 ml of CH_2Cl_2 is added at 0°C 2 ml (14 mmoles) of $(CF_3CO)_2O$. After 5 min a solution of 0.28 g (1.2 mmoles) of (VI) in 5 ml of CH_2Cl_2 is added dropwise. The reaction mixture is kept at ~20°C for 3 h, cooled to 0°C, and treated with 20 ml of a saturated aqueous soda solution. The organic layer is separated off, extracted with water (2 × 3 ml), and dried over $MgSO_4$. After evaporation of the solvent is obtained 0.17 g (70%) of (VIII), mp 97°C (cf. [15]), which according to IR spectrum and TLC is identical with an authentic sample.

In the same way was obtained 0.15 g (84%) of (IX), mp 67-69°C (cf. [16]), which according to IR spectrum and TLC is identical with an authentic sample.

4-Nitroso-3-phenylfuroxan (X). To a solution of 0.20 g (0.84 mmole) of (VI) in 7 ml of CH_2Cl_2 is added dropwise at −5°C a solution of 0.44 g (2.5 mmoles) of m-chloroperbenzoic acid in 10 ml of CH_2Cl_2. The reaction mixture is kept at the same temperature for 30 min. The precipitated m-chlorobenzoic acid is filtered off, the filtrate is extracted with a saturated aqueous $NaHCO_3$ solution (2 × 3 ml) and with water (3 ml), and dried over $MgSO_4$. After evaporation is obtained 0.15 g (93%) of (X), mp 48-50°C (dec.). IR spectrum (ν, cm^{-1}): 1600 (furox.), 1470 (NO). UV spectrum (λ, nm): 763 (NO). Mass spectrum, m/z: 191 (M^+), 161, 131, 103, 101. ^{13}C NMR spectrum (δ, ppm, $CDCl_3$): 170.89 (C–NO), 131.69, 129.28, 128.18, 120.44 (Ph), 106.87 [C=N(O)O]. ^{14}N NMR spectrum (δ, ppm, $CDCl_3$): 501.40 (NO), −13.54 (furox.).

In the same way was obtained 0.074 g (67%) of (XI), yellow liquid, decomposing at room temperature. IR spectrum (ν, cm^{-1}): 1610 (furox.), 1470 (NO). UV spectrum (λ, nm): 752 (NO). Mass spectrum, m/z: 129 (M^+), 99.69. PMR spectrum (δ, ppm, $CDCl_3$): 2.03 s (CH_3). ^{13}C NMR spectrum (δ, ppm, $CDCl_3$): 172.52 (C–NO), 97.7 [C=N(O)O], 7.75 (CH_3). ^{14}N NMR spectrum (δ, ppm, $CDCl_3$): 498.82 (NO), −11.60 (furox.).

X-ray structural analysis of (VI). Crystals of (VI) are monoclinic, at 23°C a = 24.070(7), b = 9.177(3), c = 11.380(2) Å, β = 114.76(2)°, V = 2282.58 $Å^3$, d_{calc} = 1.381 g/cm^3, Z = 8, space group C2/c.

Cell parameters and the intensities of 1799 reflections with $F^2 \geq 8\sigma$ were measured on an Enraf-Nonius CAD-4 four-circle automatic diffractometer (λMoK_α, graphite monochromator, $\theta/2\theta$ scanning $\theta \leqslant 30°$).

The structure was solved by direct methods with the MULTAN program and refined with full-matrix least-square methods, initially with isotropic and then with anisotropic approximation. The hydrogen atoms were located with the differential method and anisotropically refined. The final values of the divergence factors are R = 0.033 and R_w = 0.045. Calculations were performed on a PDP-11/23 computer with the SPD program.

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