Destructive nitration of bis(3-nitrofurazan-4-yl) disulfide

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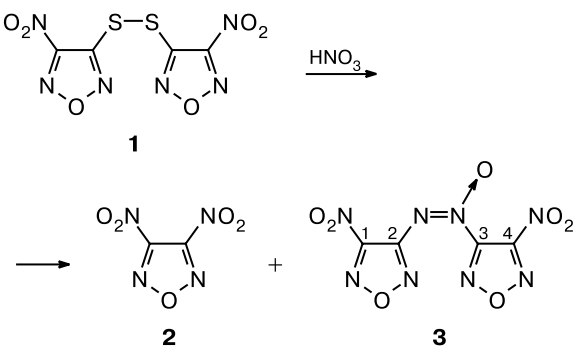
It is known that the reactions of di(het)aryl sulfides with nitric acid are accompanied by oxidation of the sulfide bridge to the sulfone one. Treatment of diaryl disulfides with nitric acid or nitrogen oxides gives rise to the corresponding mono- or di-S,S´-sulfoxides.[1]

In the present study, the disulfide bridge was shown to undergo a new type of transformations, *viz.*, destructive nitration. Treatment of bis(3-nitrofurazan-4-yl) disulfide **1**[2] with concentrated nitric acid afforded two compounds devoid of sulfur (Scheme 1). These compounds were identified as 3,4-dinitrofurazan **2**[3] and 4,4´-dinitroazoxyfurazan **3**[3—5] based on the results of spectroscopic study and TLC.

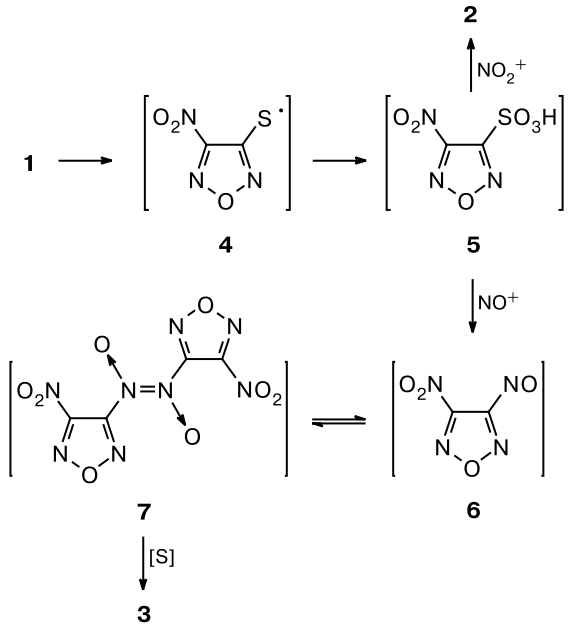
Scheme 1



It should be noted that the same two compounds are produced from 3-amino-4-nitrofurazan by oxidation with peracids[3,4] or nitration with N_2O_5.[5] The mechanism of generation of azoxy derivative **3** in these reactions assumes the intermediate formation of 3-nitro-4-nitrosofurazan. Apparently, nitration of compound **1** also proceeds through the same intermediate. The nitrosonium cation required for nitrosation can be generated in the reaction mixture due to reduction of nitric acid by divalent sulfur, the latter being generally oxidized to the hexavalent state.

The assumed sequence of transformations of compound **1** into products **2** and **3** is shown in Scheme 2. Presumably, the first step of this process involves the cleavage of the S—S bond to form sulfenyl radical **4**. The sulfur atom in the latter is oxidized in the reaction medium to give sulfonic acid **5**. Substitutive nitration of the sulfo group affords nitro product **2**. Nitrosation is accompanied by the formation of nitroso compound **6**, which, like other nitrosofurazans,[6] undergoes dimerization to diazene dioxide **7**. Reduction of one N-oxide function in compound **7**, for example, with low-valence sulfur gives rise to product **3**.

Scheme 2



By contrast, bis(3-nitrofurazan-4-yl) sulfide **8**,[2] in which a weak S—S bond is absent, is not cleaved with nitric acid. Even after refluxing in concentrated nitric acid for 1 h, the major portion of compound **8** (84%) remained intact, and the reaction afforded products of oxidation of the sulfur atom in thioether **8**, such as sulfoxide **9**[2] and sulfone **10**,[2] in low yields (7 and 5%, respectively) (Scheme 3).

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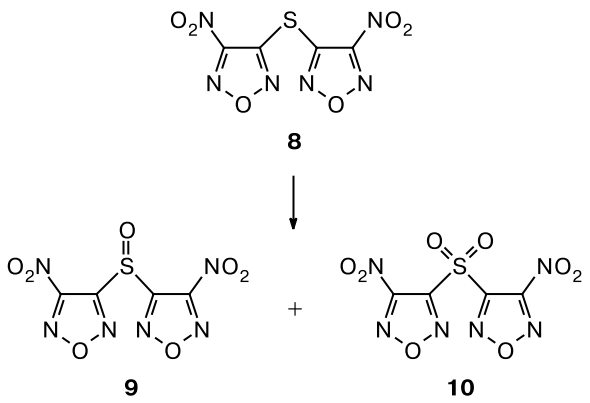
Scheme 3



Disulfide **1** (2.9 g, 0.01 mol) was added portionwise with vigorous stirring to nitric acid (ρ = 1.5 g cm^{-3}, 30 mL) at 35—40 °C. Then the temperature was slowly raised to 60 °C, after which the reaction mixture was stirred for 3 h, cooled, and poured onto ice. The resulting emulsion was extracted with CH_2Cl_2 (3×30 mL). The extract was dried with $MgSO_4$ and concentrated. Chromatography of the residue on silica gel (SiO_2 40/100, a 3 : 1 CH_2Cl_2 : pentane mixture as the eluent) gave two fractions. First fraction, compound **2**;[3] the yield was 0.7 g (22%), m.p. −15 °C, b.p. 168 °C. MS, *m/z*: 160 $[M]^+$, 114 $[M - NO_2]^+$, 98 $[M - O - NO_2]^+$, 68 $[M - 2\,NO_2]^+$. ^{13}C NMR (CD_2Cl_2), δ: 152.9. ^{14}N NMR (CD_2Cl_2), δ: −44.0 ($\underline{N}O_2$). Second fraction, azoxy derivative **3**;[3—5] the yield was 0.96 g (35%), m.p. 111.5—112 °C. MS, *m/z*: 272 $[M]^+$, 256 $[M - O]^+$, 226 $[M - NO_2]^+$, 210 $[M - O - NO_2]^+$. ^{13}C NMR (acetone-d_6), δ: 149.8 (C(2)); 153.6 (C(3)); 155.2 (C(4)); 157.4 (C(1)). ^{14}N NMR (acetone-d_6), δ: −37.2 ($\underline{N}O_2$), −41.6 ($\underline{N}O_2$), −69.6 ($\underline{N}\rightarrow O$).

The ^{13}C and ^{14}N NMR spectra were recorded on a Bruker AM-300 spectrometer operating at 75.4 and 21.5 MHz, respectively, at natural isotope abundance. The chemical shifts in the ^{14}N NMR spectra are given in the δ scale relative to nitromethane as the external standard. The mass spectra were measured on Finnigan MAT INCOS-50 and Varian MAT CH-111 instruments (EI, 70 eV). The course of the reactions and the purities of the products were monitored by TLC on Silufol UV-254 plates using a pentane —CH_2Cl_2 mixture as the eluent; visualization was carried out with UV light or by spraying with a 5% diphenylamine solution in hexane.

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References

1. Y. Ogata, in *Oxidation in Organic Chemistry*, Ed. W. S. Trahanovsky, Academic Press, New York—San Francisco—London, 1978, **5**, Part C, 338—342.
2. A. B. Sheremetev, E. V. Mantseva, N. S. Aleksandrova, V. S. Kuzmin, and L. I. Khmel´nitskii, *Mendeleev Commun.*, 1995, 25.
3. T. S. Novikova, T. M. Melnikova, O. V. Kharitonova, V. O. Kulagina, N. S. Aleksandrova, A. B. Sheremetev, T. S. Pivina, L. I. Khmelnitskii, and S. S. Novikov, *Mendeleev Commun.*, 1994, 138.
4. A. Gunasekaran, M. L. Trudell, and J. H. Boyer, *Heteroatom Chem.*, 1994, **5**, 441.
5. A. M. Churakov, S. E. Semenov, S. L. Ioffe, and V. A. Tartakovsky, *Mendeleev Commun.*, 1995, 102.
6. A. B. Sheremetev, T. S. Novikova, T. M. Mel´nikova, and L. I. Khmel´nitskii, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1990, 1193 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1990, **39**, 1073 (Engl. Transl.)].

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