Brief Communications

Polyazoxyfurazans in reactions with ammonia*

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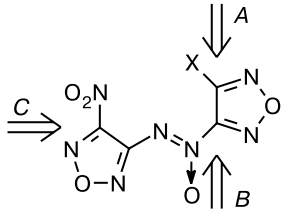
The reaction of 4,4′-bis(4-nitrofurazan-3-yl-*NNO*-azoxy)azoxyfurazan with ammonia affords a product of nucleophilic substitution for the furazanyldiazene oxide fragment, while the nitro groups remain intact.

Key words: furazans, azoxyfurazans, aminofurazans, nitrofurazans, nucleophilic substitution, NMR spectroscopy.

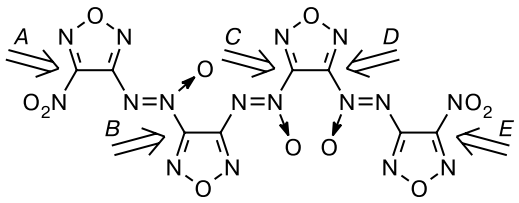
Earlier,[2] we showed that the reactions of 4,4′-dinitroazoxyfurazan (**1**) with nucleophiles, including ammonia, predominantly occur at two reaction centers (*A* and *B*) to give products of substitution for nitro and furazanyldiazene oxide groups, respectively. Compound **1** is only slightly consumed in the reaction at center *C*. Competitive reactions at these centers yield five products. In 4-chloro-3-(4-nitrofurazanyl-*NNO*-azoxy)furazan (**2**), nucleophilic substitution involves only nitro and furazanyldiazene oxide groups, while the chlorine atom remains intact.[3] In this case, however, the reaction at center *C* becomes dominant.



1, **2**

X = NO_2 (**1**), Cl (**2**)

In continuation of the investigations of nucleophilic substitution in nitroazoxyfurazans, we studied a reaction of compound **3** [4] with ammonia. Compound **3** contains five potential reaction centers (*A*—*E*), and hence more than ten products could be expected.



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However, we found that treatment of polyazoxy compound **3** with a solution of ammonia in chloroform affords only two products (Scheme 1). Both compounds were purified chromatographically and then thoroughly studied by spectroscopic methods. One of the products, which was formed by nucleophilic substitution at cen-

* For the preceding publication concerning this topic, see Ref. 1.

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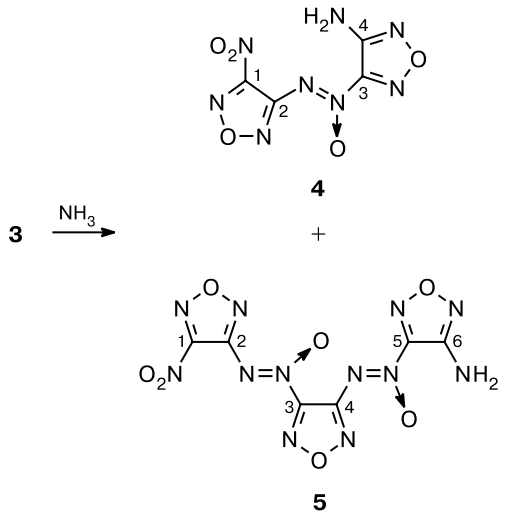
ter *C*, contains two furazan rings and is identical with the known[2] compound **4**. The other product **5** obtained in pathway *D* contains three furazan rings.

Scheme 1



The total yield of the products was 92—96%. Both compounds were formed as a result of nucleophilic substitution at the same furazan ring containing two azoxy groups attached to it through the N atoms of the N(O) fragments. Thus, the furazanyldiazene oxide groups in compound **3** are more labile than the nitro groups. Note that, as in most of the previously studied[2,3,5–7] reactions, no products formed by the leaving group were isolated.

A mutual arrangement of the nitro and azoxy groups was determined from ^{13}C and ^{14}N NMR data with consideration of the known patterns.[5,8] Signals for the C atoms bound to the nitro group and to the N atom of the N(O) fragment of the azoxy group are broadened because of a $^{13}C—^{14}N$ coupling. The N atoms of the N(O) fragment of the azoxy group were located by selective double $^{13}C—\{^{14}N\}$ heteronuclear resonance.

Experimental

Melting points were determined on a Kofler stage. Natural-isotope ^{13}C and ^{14}N NMR spectra were recorded on a Bruker AM-300 spectrometer (75.4 and 21.5 MHz, respectively) in acetone-d_6. Chemical shifts in ^{14}N NMR spectra are given on a δ scale relative to nitromethane as the external standard. Mass spectra were recorded on Finnigan MAT INCOS-50 and Varian MAT CH-111 instruments (EI, 70 eV). IR spectra were recorded on a Specord IR-75 spectrometer (pellets with KBr). The course of the reaction was monitored and the purity of products was checked by TLC with benzene as an eluent on Silufol UV-254 plates (spots are visible under UV light; visualization can also by spraying the plates with a 5% solution of diphenylamine in hexane with subsequent heating or irradiation with a UV lamp; azoxyfurazans appear as dark spots). For preparative chromatography, SiO_2 40/100 was used.

Reaction of 4,4′-bis(4-nitrofurazan-3-yl-*NNO*-azoxy)azoxyfurazan (3) with NH_3. A 0.2 M solution of NH_3 (30 mL) in $CHCl_3$ was added at ~20 °C to a stirred solution of compound **3**[4] (0.99 g, 2 mmol) in 350 mL of $CHCl_3$. The reaction mixture was kept at ~20 °C for 1 h, washed with cold water (3×150 mL), dried with $MgSO_4$, filtered, and concentrated at a reduced pressure. The residue was purified by column chromatography.

First fraction: **3-amino-4-(4-nitrofurazan-3-yl-*NNO*-azoxy)furazan (4)**; the yield was 0.25 g (51%), yellow crystals, m.p. 131 °C (*cf.* Ref. 2: m.p. 130—131 °C). MS, *m/z*: 242 $[M]^+$, 226 $[M - O]^-$, 196 $[M - NO_2]^+$, 180 $[M - O - NO_2]^+$. ^{13}C NMR, δ: 149.5 (C(2)); 151.9 (C(4)); 152.9 (C(3)); 157.4 (C(1)). ^{14}N NMR, δ: −36.4 ($\underline{N}O_2$); −59.3 ($\underline{N}\rightarrow O$).

Second fraction: **4-(4-aminofurazan-3-yl-*N(O)N*-azoxy)-3-(4-nitrofurazan-3-yl-*NNO*-azoxy)furazan (5)**; the yield was 0.3 g (42%), yellow crystals, m.p. 98—99 °C. Found (%): C, 20.31; H, 0.56; N, 47.49. $C_6H_2N_{12}O_7$ (M 354.16). Calculated (%): C, 20.35; H 0.57; N, 47.46. MS, *m/z*: 354 $[M]^+$, 338 $[M - O]^+$, 271, 254, 158, 142. IR, ν/cm^{-1}: 3460, 3390, 3330, 1620, 1550, 1480, 1420, 1350, 1180, 1150, 1020, 930, 820. ^{13}C NMR, δ: 149.9 (C(2)); 150.0 (C(4)); 152.3 (C(6)); 153.0 (C(3)); 156.4 (C(5)); 157.4 (C(1)). ^{14}N NMR, δ: −36.9 ($\underline{N}O_2$); −58.5 (C(5)—$\underline{N}\rightarrow O$); −63.8 (C(3)—$\underline{N}\rightarrow O$).

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