4-Hydroxy-3-(α-nitroalkyl-ONN-azoxy)furazans and some their O-derivatives*

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Methods for the synthesis of 4-hydroxy- and 4-alkoxy-3-(α-nitroalkyl-ONN-azoxy)furazans and difurazanyl ethers were developed. The methods involve displacement of the nitro group from 4-nitro-3-(α-nitroalkyl-ONN-azoxy)furazans under the action of aqueous solutions of alkalis, mono- and diatomic alcohols (in the presence of inorganic bases), and sodium carbonate in anhydrous acetonitrile.

Key words: furazans, (α-nitroalkyl-ONN-azoxy)furazans, 4-hydroxy-3-(α-nitroalkyl-ONN-azoxy)furazans, 4-alkoxy-3-(α-nitroalkyl-ONN-azoxy)furazans, 3,3′-bis(α-nitroalkyl-ONN-azoxy)difurazanyl ethers, nitrofurazans, hydroxyfurazans, nucleophilic substitution.

Earlier, the syntheses of 4-amino-3-(α-nitroalkyl-ONN-azoxy)furazans1 and their high-energy derivatives (including new oxidants 3-(polynitromethyl-ONN-azoxy)-4-nitraminofurazans) have been reported.2 As a next step in those investigations, here we studied nucleophilic substitution of the nitro group in a series of 4-nitro-3-(α-nitroalkyl-ONN-azoxy)furazans under the action of O-nucleophiles. The goal of the present work was to obtain 4-hydroxy-3-(α-nitroalkyl-ONN-azoxy)furazans that could serve as intermediate products in the synthesis of high-energy compounds with potential attractive properties.

Results and Discussion

Nitrofurazans are known to undergo nucleophilic substitution in reactions with aqueous solutions of alkalis3 to give hydroxyfurazans. We found that 4-nitro-3-(α-nitroalkyl-ONN-azoxy)furazans 1—3 react with alkalis in water and a water-miscible organic solvent (acetone or acetonitrile) even at 0—3 °C and that the nitro group directly bound to the furazan ring is replaced by a hydroxy group in 0.5 h. Treatment of the reaction mixture with HCl gives the desired products 4-hydroxy-3-(α-nitroalkyl-ONN-azoxy)furazans 4—6 (Schemes 1 and 2).

With substrate 3, the above transformation is complicated by hydrolysis of the 2,2-dimethyl-5-nitro-1,3-dioxan-5-yl substituent upon the treatment with HCl, yielding triol 6 (see Scheme 2).

4-Hydroxy-3-(α-nitroalkyl-ONN-azoxy)furazans 5 and 6 are yellow oils, while product 4 is a white crystalline solid with m.p. 85.0—87.0 °C. Hydroxyfurazans 4 and 5 can form metal salts by exchanging the OH proton. For instance, treatment of compound 4 with EtONa in diethyl ether affords the sodium salt Na[4].

The reaction in methanol in the presence of inorganic bases proceeds even more violently than that in aqueous

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solutions of alkalis. Although nitrofurazans 1—3 do not react even with boiling methanol when it is used alone, addition of K₂CO₃ or KOH promotes nucleophilic displacement of the nitro group from the furazan ring by a methoxy group. The reaction at 20 °C is completed in 0.5 h to give the corresponding 4-methoxy-3-(α-nitroalkyl-ONN-azoxy)furazans 7—9 (Scheme 3). Note that the use of K₂CO₃ ensures higher yields of the reaction products than does KOH (e.g., 92 against 81% for compound 9).

Reactions of 4-nitro-3-(α-nitroalkyl-ONN-azoxy)furazans 1 and 3 with such a strong nucleophile as MeONa in methanol at 20 °C unexpectedly resulted in replacement of both the nitro groups, thus producing 4-methoxy-3-(α-methoxyalkyl-ONN-azoxy)furazans 10 and 11, respectively (Scheme 4).

The structures of the methoxy and dimethoxy derivatives 7—11 were confirmed by ¹H, ¹³C, and ¹⁴N NMR spectra. Comprehensive assignment of the signals in the ¹³C NMR spectra of these compounds was performed using 2D NMR experiments (¹H—¹³C HMBC).

Methoxyfurazans 7—9 and 11 are white crystalline compounds. Interestingly, the replacement of the nitro group in the (α-nitroalkyl-ONN-azoxy) fragment by the methoxy group lowers the melting point (from 78.5—79.0 and 72.5—73.0 °C for 9 and 7, respectively, to 48.0—49.5 °C for dimethoxy derivative 11). Compound 10 is entirely liquid at room temperature.

Like other nitrofurazans,⁴ 4-nitro-3-(α-nitroalkyl-ONN-azoxy)furazans react with glycols in the presence of bases to give glycol mono- and diethers. For instance, a reaction of an excess of compound 3 with ethylene glycol in acetonitrile in the presence of K₂CO₃ at 20 °C takes 96 h, affording diether 12 (Scheme 5). Monoether 13 is also formed as a by-product (7%), even when nitrofurazan 3 is employed in more than a twofold excess.

4-Nitro-3-(α-nitroalkyl-ONN-azoxy)furazans also react with weak bases in anhydrous media, which is typical of nitrofurazans.⁵,⁶ Treatment of compound 3 with Na₂CO₃ in anhydrous acetonitrile (60—65 °C, 5 h) gives difurazanyl ether 14 in 63% yield (Scheme 5). This product is a white crystalline solid with m.p. 99.0—100.0 °C.