3-Amino-4-(α-nitroalkyl-ONN-azoxy)furazans and some of their derivatives

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Synthetic procedures towards 3-amino-4-(α-nitroalkyl-ONN-azoxy)furazans and their derivatives involving nucleophilic displacement of the nitro group of 3-nitro-4-(α-nitroalkyl-ONN-azoxy)furazans on treatment with ammonia, primary and secondary amines, including diamines, were developed.

Key words: furazans, (α-nitroalkyl-ONN-azoxy)furazans, 3-amino-4-(α-nitroalkyl-ONN-azoxy)furazans, nitrofurazans, aminofurazans, nucleophilic substitution.

Earlier, we have developed method for the synthesis of bis(α-nitroalkyl-ONN-azoxy)furazans and their derivatives by the reaction of 3,4-diaminofurazan with geminal nitronitroso compounds in the presence of dibromoiso-cyanuric acid (DBI). Despite the moderate yields (20—55%) of the aforesaid compounds and stability of the intermediates, 3-amino-4-(α-nitroalkyl-ONN-azoxy)furazans, the latter were not obtained in preparative yields even after changing the reaction conditions. Since the compounds of this type are of interest and could be used as half-products towards other energetic compounds, in the present work we suggest another strategy for their synthesis. The approach involved the nucleophilic displacement known for the furazans—namely, the displacement of the nitro group on the furazan ring by N-nucleophiles. It was found that 3-nitro-4-(α-nitroalkyl-ONN-azoxy)furazans and some of their derivatives (compounds 1—3) reacted rather smoothly with ammonia at room temperature in the inert solvents to give target 3-amino-4-(α-nitroalkyl-ONN-azoxy)furazans 4—7 (Scheme 1).

On going from ammonia to methylamine, the reaction (performed in H₂O—CH₂Cl₂) proceeded more readily. It is of note that disubstitution products 8—9 were predominantly formed in the reactions with diamines carried out even with the large excess of the latter (Scheme 2).

However, we were not able to extend this procedure on the aromatic amines (the reactions were carried out on the example of p-toluidine); no formation of the substitution product was observed.

In our opinion, these results indicate that electronic effect (electron-withdrawing or electron-releasing) of the α-nitroalkyl substituent at the ONN-azoxy group does not affect the nucleophilic substitution of the nitro group on the furazan ring. It is true only when the substituent is stable upon the nucleophilic attack or transforms into stable structural fragment.

Thus, no individual products of the reaction of 3-(dibromonitromethyl-ONN-azoxy)-4-nitrofurazan and 3-(2-hydroxy-1-hydroxymethyl-1-nitroethyl-1-ONN-azoxy)-4-nitrofurazan with ammonia were isolated, although in
the latter case the target product of the displacement of the nitro group (i.e., compound \( \text{10} \)) is rather stable and was prepared by solvolysis of aminofurazan \( \text{6} \) (Scheme 3).

Scheme 3

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\begin{align*}
\text{6} & \quad \text{AcCl, MeOH} \quad \text{HN}_{\text{O}} \quad \text{N} \quad \text{N} \\
& \quad \text{(HOH}_{2}\text{C})_{2}\text{C} \quad \text{N} \quad \text{N} \quad \text{NH}_{2} \\
& \quad \text{10} \\
& \quad \text{AcCl, MeOH} \\
\end{align*}
\]

Reaction of 3-(dinitromethyl-ONN-azoxy)-4-nitrofurazan (\( \text{11} \)) with ammonia proceeded in two steps. In \( \text{CH}_{2}\text{Cl}_{2} \) after 2 min of the reaction, ammonium salt \( \text{11-NH}_{4} \) was formed in 90% yield. This salt also formed on bubbling of \( \text{NH}_{3} \) through a solution of \( \text{11} \) in \( \text{MeCN} \) and then within 2.5 h transformed into ammonium salt of 3-amino-4-(dinitromethyl-ONN-azoxy)furazan (\( \text{12-NH}_{4} \)) in 95% yield (Scheme 4). Compound \( \text{12-NH}_{4} \) was obtained in a yield of 78% in two steps also (denitration and ammonolysis) by treatment of 3-nitro-4-(trinitromethyl-ONN-azoxy)furazan (\( \text{13} \)) with ammonia.

Treatment of salt \( \text{12-NH}_{4} \) with gaseous \( \text{HCl} \) in \( \text{MeOH} \) afforded low stable crystalline 3-nitro-4-(dinitromethyl-ONN-azoxy)furazan (\( \text{12} \)) with m.p. 85—87.5 °C (decomp.).

Likewise ammonia, methylamine reacted with \( \text{11} \). In this reaction due to the higher reactivity of methylamine with respect to ammonia, after methylammonium salt formation bearing the dinitromethyl group, a product of substitution of the methylamino group for the nitro group immediately formed. Treatment of this product with \( \text{HCl} \) resulted in 3-(N-methylamino)-4-(dinitromethyl-ONN-azoxy)furazan (\( \text{14} \)). For purification and unambiguous identification, furazan \( \text{14} \) was converted into more stable potassium salt \( \text{14-K} \) by treatment with \( \text{KOH} \) in \( \text{MeOH} \) (Scheme 5).

Compound \( \text{11} \) reacted with ethylenediamine similarly but with lower rate to give (after acidification) a product at both the amino group of ethylenediamine, \( N,N' \)-bis-[4-(dinitromethyl-ONN-azoxy)furazan-3-yl]ethylenedi-