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# Reaction of nitrosolic acid salts with dinitrogen tetraoxide*

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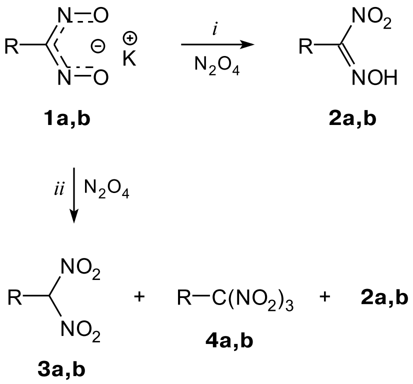
It is known that the reactions of salts of various α,α-dinitromethyl compounds with $N_2O_4$ in inert organic solvents afford the corresponding trinitromethyl derivatives and/or nitrolic acids, furoxans, and nitriles.[1—13] The first step of this process is the nitrosation of the dinitromethyl anion leading to the α,α-dinitro-α-nitrosomethyl intermediate,[2,5,6,8,12] which is transformed into this or another product depending on the reaction conditions. Literature data on the reaction of salts of α,α-dinitrosomethyl compounds (nitrosolic acid salts) with $N_2O_4$ are missing, and only few reactions of nitrosolic acids are known.

We found that the treatment of a suspension of alkylnitrosolic acid salt **1a,b** with one equivalent of $N_2O_4$ in acetonitrile or diethyl ether at –10 °C resulted in the smooth formation of the corresponding nitrolic acid **2a,b**, which can be isolated in 80—85% yield (Scheme 1).

**Scheme 1**

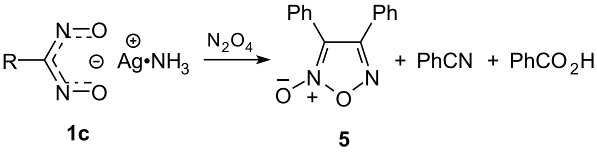


R = Me (**a**), Et (**b**).
*i*. 1 equiv.; *ii*. > 2 equiv.

A mixture of nitrolic acid **2a,b** with di- (**3a,b**) and trinitroalkanes (**4a,b**) (total yield ~75%, ratio 2 : 3 : 1, respectively) is formed when the amount of $N_2O_4$ is increased to 2 equivalents (see Scheme 1). The further increase in $N_2O_4$ excess (up to 10 equivalents) results in the complete consumption of nitrolic acids to subsequent transformations, whereas dinitroalkanes **3a,b** still remain in the reaction mixture (up to ~4%). However, the total yield of the nitro derivatives also decreases to 40—48% (the amount of such by-products as RCN and RCOOH increases in the reaction mixture).

It turned out that the single product bearing the N—O bond and formed by the treatment of phenylnitrosolic acid silver ammoniate salt **1c** (other salts of this acid are unknown) with $N_2O_4$ in diethyl ether at –10 °C is 3,4-diphenylfuroxan **5** (Scheme 2). The maximum yield (62%) of compound **5** is achieved when using two equivalents of $N_2O_4$, and benzonitrile (3—15%) and benzoic acid (5—20%) are always formed as by-products.

**Scheme 2**



The reaction of the salt of simplest nitrosolic acid **1d** with nitrogen dioxide is most complicated. In this case, depending on the reactant ratio, temperature, and solvent, the reaction mixture contains up to twenty different products (detected by TLC and NMR). Selected probable processes occurring in the reaction mixture are shown in Scheme 3. It should be mentioned that the oxidation and nitrosation reactions are main in this scheme. The intermediate formation of formonitrile oxide **6** is confirmed by the formation of its trimer **7** and tetramer **8** (see Ref. 14), which is characteristic of this compound.[15]

Compounds **3d**, **4d**, **7**, and **8** were isolated in the individual state by chromatography or other preparative methods.

By analogy to the reaction of salts of dinitromethyl compounds with $N_2O_4$ (see above), we could expect the primary nitrosation of nitrosolic acid salts, which would afford trinitrosomethyl compounds (trinitrosomethane **9** is their simplest representative). However, all our attempts to detect the formation of nitrosoform **9** or its analogs in

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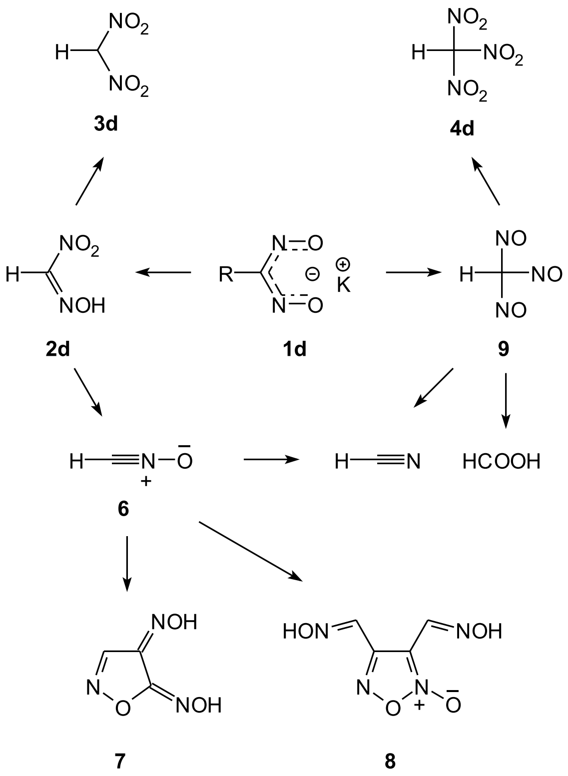
**Scheme 3**



the reactions of compounds **1a—c** with $N_2O_4$ under the indicated conditions were unsuccessful.

Thus, although the reaction of salts of α,α-dinitrosomethyl compounds with $N_2O_4$ resembles the analogous reaction of dinitromethyl compound salts, it has its own unique transformations routes depending on both the substituent type in the starting compound and reaction conditions. It seems important to find synthetic possibilities of the use of α,α-dinitrosomethyl compounds for the development of chemistry of compounds bearing several groups including the N—O fragment at the same carbon atom.

The starting salts **1a—d**,[16] as well as the authentic samples of products **2a**,**b**,[17] **3a—d**,[18] **4a**,**b**,[19] and **5**,[6] were synthesized according to known procedures. The reaction mixtures were analyzed by TLC (Silufol UV 254 plates) and $^1H$, $^{13}C$, and $^{14}N$ NMR spectroscopy on a Bruker AM-300 spectrometer with the working frequencies 300.13, 75.7, and 21.5 MHz, respectively (the reactions were carried out in an NMR tube in $CD_3CN$).

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