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Generation of Nitro Formonitrile Oxide as an Intermediate for the Preparation of Dinitrofuroxan

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Two methods for the generation of nitro formonitrile oxide (NFNO) have been proposed: dehydration of dinitromethane and nitration of 1-nitro-2-methylprop-1-ene; NFNO has been identified in the form of its cyclodimerization product, dinitrofuroxan (DNFO).

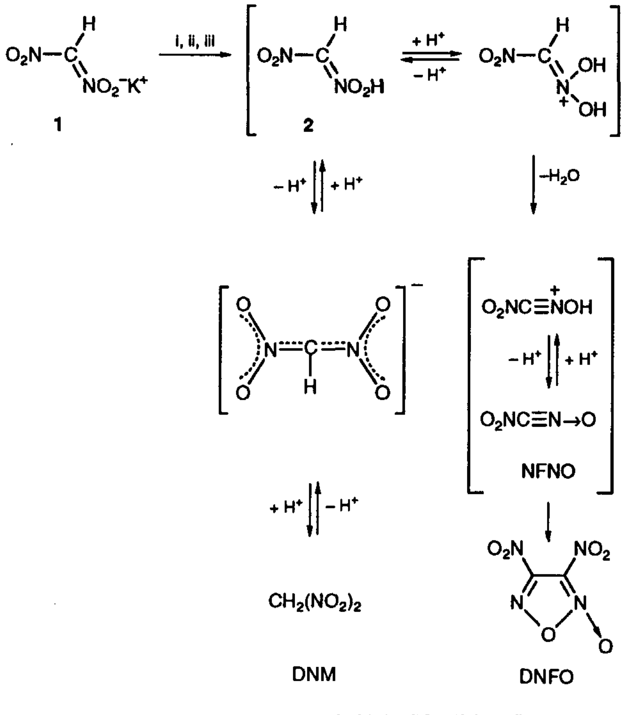
Previously[1,2] we proposed a new method for the generation of nitrile oxides by reaction of N_2O_4 with salts of substituted dinitromethanes. This method has, however, proved unsuitable for the preparation of nitro formonitrile oxide (NFNO) from the potassium salt of trinitromethane (TNM). Several attempts at the generation of NFNO have been described in the literature. Its intermediate formation was suggested in a theoretical consideration of dinitromethane (DNM) thermodestruction,[3] as well as in experimental work on acylation of its salts[4] and trimethylsilylation of methyl nitroacetate, DNM[5] and TNM,[6] but in no case was any evidence of its formation obtained.

In this work the possibility of generating NFNO by other methods has been investigated, *viz.* dehydration of DNM and nitration of acetyl methanenitrolic acid and 1-nitro-2-methylprop-1-ene.

The dehydration of the primary nitro compounds is a rather widespread method for the preparation of nitrile oxides. From the reagents used earlier for this purpose we have chosen concentrated H_2SO_4 and oleum because this enabled us to use for the dehydration not the free DNM, but its potassium salt **1**, which is more accessible and convenient to handle. The latter at the start of its reaction with H_2SO_4 should give DNM in the *aci*-form **2**, which according to ref. 8 is a necessary step for this method of nitrile oxide generation. Concentrated H_2SO_4 of known strength is known[9] to briefly stabilize the *aci*-form of polynitroalkanes.

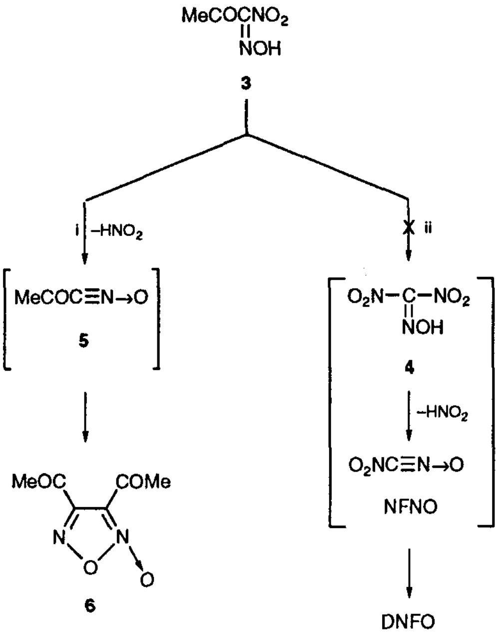
In this way, **1** when treated with concentrated H_2SO_4 or oleum could presumably give rise to both NFNO on account of dehydration of **2** and to the free DNM on account of a transition of **2** to the true nitro compound. Since the rate of nitrile oxide cyclodimerization to furoxan grows in parallel with the electron-accepting effect of the substituent[10] we expected that the main direction of NFNO transformation would be its cyclodimerization to dinitrofuroxan (DNFO). In our opinion DNFO registration may be considered as direct evidence of NFNO generation.

In fact, the reaction of **1** with 95% H_2SO_4 at 20 °C gave DNFO and DNM in a 12:88 molar ratio, their total yield accounting nearly quantitatively for the initial **1**. Thus, the yield of DNFO may be regarded as almost 100% for DNM having undergone dehydration. Oleum (30%) at 20 °C turned out to be a better dehydrating reagent than 95% H_2SO_4. In this case the molar ratio for the DNFO and DNM obtained amounted to 28:72 (with the quantitative total yield as well). The free DNM did not change under these conditions. The ratio of the DNFO and DNM obtained was determined from a plot of n_D^{20} for the binary mixture DNFO[11]–DNM[12] *versus* its composition.[†] Heating the reaction mixture obtained from **1** and 95% H_2SO_4 at 100 °C gave only DNFO in 34% yield. In this case the yield was presumably still higher, but part of the product may have decomposed under the experimental conditions. A special experiment actually showed DNFO to decompose when heated in H_2SO_4 at 100 °C. The DNFO yield growth upon transition from i to ii may indicate the ability of DNM to pass to its *aci*-form when heated in concentrated H_2SO_4 (Scheme 1).



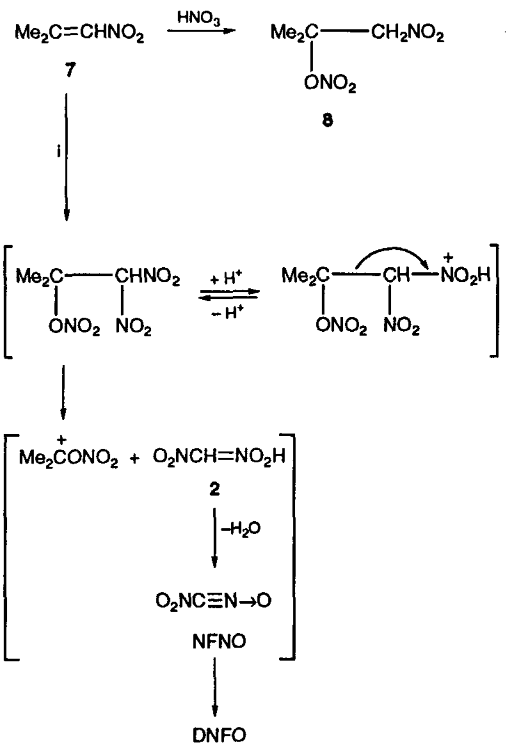
Scheme 1 *Reagents and conditions:* i, 95% H_2SO_4 (26 mol), *n*-pentane, 20 °C, 4 min; ii, as in i, then 100 °C, 1 h; iii, 30% oleum (6 mol of SO_3), *n*-pentane, 20 °C, 4 min.

[†] DNM yield in the mixture was also determined by ^1H NMR spectroscopy[12] (1,3,5-trinitro-1,3,5-triazahexane as an internal standard) and DNFO yield—by ^{14}N NMR spectroscopy[11] (tetranitromethane as an internal standard). The result is in a good agreement with yields based on the n_D^{20} value of the mixture.



Scheme 2 *Reagents and conditions:* i, 26% HNO_3, 50 °C, 30 min; 80 °C, 10 min, **6** (93%); ii, 100% HNO_3 (10 mol), NH_4NO_3 (10 mol), 20 °C, 2 h, **3** (90%).

One of the methods for nitrile oxide generation is to split off HNO_2 from nitrolic acids.[13,14] Using the conditions already described we tried to carry out a desubstitution–nitration of acetyl methanenitrolic acid **3**, assuming that the dinitro formaldoxime **4** to be formed would lose HNO_2 to give NFNO. Under these conditions,[14] however, **3** remained unnitrated, whereas under the conditions of the method in ref. 13 it lost HNO_2 to give acetyl formonitrile oxide **5**, which cyclodimerized to diacetylfuroxan **6**[15] (Scheme 2).



Scheme 3 *Reagents and conditions:* i, N_2O_5 (1 mol), 100% HNO_3, 0–20 °C, 2 h, DNFO (50%). Reactions were carried out with mixing and the products were isolated by extraction after pouring the reaction mixture into ice-water.

A successful attempt to generate NFNO by nitration proved to be the one applied to 1-nitro-2-methylprop-1-ene **7**, a structural analogue of alkyl β,β-dimethylacrylates, which give diesters of furoxandicarboxylic acid by nitration with 100% HNO_3.[16] We investigated HNO_3–H_2SO_4 mixtures, 100% and 90% HNO_3, N_2O_5 and NO_2BF_4 as nitrating reagents. DNFO formation was observed only in nitrating media based on a 100% HNO_3: HNO_3–H_2SO_4 mixture, 100% HNO_3, N_2O_5–HNO_3 mixture, the latter being the best nitrating reagent. Concurrently addition of HNO_3 to the double bond of **7** takes place to give a fair amount of 1-nitro-2-methylpropan-2-ol nitrate **8** (Scheme 3).

In summary, NFNO generation can be brought about by methods similar to those used for the preparation of other nitrile oxides. The structure of DFNO resulting from NFNO cyclodimerization was confirmed by a comparison of its physical and spectral characteristics with those of the specimen synthesized first by our colleagues.[11]

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