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3,4-Dinitrofuroxan—the First Example of a Pernitro Heterocycle

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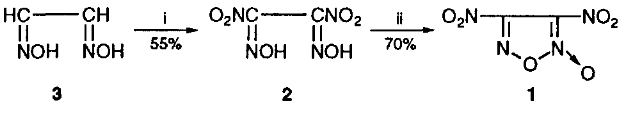
A pernitrofuroxan–3,4-dinitrofuroxan–has been synthesized for the first time, and nucleophilic substitution studies show this compound to be a starting material for the synthesis of 4-functionally substituted 3-nitrofuroxans not hitherto readily accessible.

Pernitro heterocycles are not known to date, and their existence or stability still remains an open question. These compounds could be of interest not only theoretically, but also in organic synthesis; *e.g.*, the nitro group activated by other nitro groups in such structures should easily undergo nucleophilic substitution giving rise to a series of substances. A representative of this kind of structure is 3,4-dinitrofuroxan **1**.

The most widely known method for the introduction of a nitro group into aromatic and heterocyclic systems is the oxidation of an amino group. This can not, however, be applied to the preparation of **1** because the appropriate amino derivatives are missing. Therefore, we decided to form the furoxan ring based on a suitable compound with two nitro groups. Dinitroglyoxime **2** was obtained by nitration of glyoxime **3** with 25% nitric acid in ether and then transformed into **1** by oxidation with dinitrogen tetroxide in carbon tetrachloride (Scheme 1).†



Scheme 1 *Reagents and conditions:* i, 25% HNO_3 (3 mol), Et_2O, 18 °C, 2.5 h; ii, N_2O_4 (5 mol), CCl_4, 20 °C, 3.5 h.

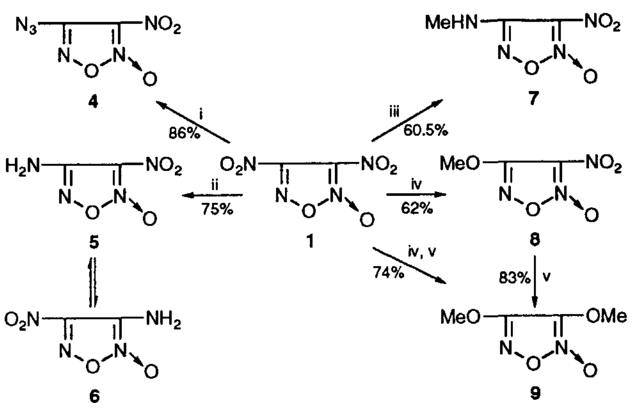
Compound **1** is a mobile liquid of slightly yellow colour and pungent odour, which decomposes slowly at ambient temperature, but can be stored at -15 to -20 °C without change; **CAUTION! 1** is of explosive nature and should be handled with care.

The nitro group in nitrofuroxans is known to be prone to substitution by a nucleophile at the 3[1] as well as at the 4[1–5] positions. The relative capability of nitro groups to be substituted at the 3 and 4 positions has remained an open question. Compound **1** is a unique furoxan compound containing nitro groups at both the 3 and 4 positions simultaneously.

We have shown that the nitro group at the 4 position is the first to leave by nucleophilic substitition at position 1. The second nitro group is substituted only by action of strong nucleophiles. Thus, **1** is a starting material for the synthesis of 4-functionally substituted 3-nitrofuroxans hitherto inaccessible (Scheme 2).† The structure of the compounds synthesized has been proved by ^{13}C NMR spectroscopy, whose signals were assigned in the same way as for isomeric nitrophenylfuroxans.[6]

When a solution of **5** in organic solvents is stored at 18–20 °C, an equilibrium mixture of isomers is formed, with a stable composition, containing 30% of **6** as judged by ^{14}N NMR spectroscopy.

With **9** as an example it was shown that the two nitro groups in **1** can be substituted by alkoxy groups in a ratio of reagents 1:2. When other nucleophiles (weaker ones) are used the nitro group at the 3 position is not replaced.



Scheme 2 *Reagents and conditions:* i, NaN_3 (3 mol), anhydrous AcOH, 20 °C; ii, NH_3, CH_2Cl_2, -20 °C; iii, $MeNH_2$ (1 mol), as for ii; iv, MeOH, NaOH (1 mol), -25–15 °C; v, MeOH, NaOH (1 mol), 10 °C.

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† All new compounds synthesized have satisfactory elemental analysis data and are characterized by ^{1}H and ^{13}C NMR spectroscopic data.

1 $n_D^{20} = 1.5375$, d_4^{20} 1.71 g cm^{-3}, MR_D calc. 30.14, MR_D found 32.27, $\Sigma R = +2.13$, ^{13}C NMR 122.7 ($O_2NC{=}N{-}O$) and 153.6 ($O_2NC{=}N$), ^{14}N NMR ($CDCl_3$) -42.57 (4–NO_2) and -47.72 (3–NO_2).

2 M.p. 84–84.5 °C (decomp.), unstable when stored, especially in a closed vessel, ^{1}H NMR [$(CD_3)_2CO$] 6.8 (OH), ^{13}C NMR [$(CD_3)_2CO$] 148.27, ^{14}N NMR -25.11 (NO_2).

4 M.p. 40–43 °C, ^{13}C NMR [$(CO_3)_2CO$] 128.3 (C–NO_2) and 148.1 (C–N_3). (**CAUTION; Explosive**).

5 M.p. 40–43 °C, ^{13}C NMR ($CDCl_3$) 128.0 (C–NO_2) and 152.3 (C–NH_2), ^{14}N NMR [$(CD_3)_2CO$] -34.30 (NO_2).

6 ^{13}C NMR ($CDCl_3$) 126.7 (C–NO_2) and 158.0 (C–NH_2), ^{14}N NMR [$(CD_3)_2CO$] -31.38 (NO_2).

7 M.p. 89–90 °C, ^{1}H NMR ($CDCl_3$) 3.1 d (3H, Me), 5.7 m (NH), ^{13}C NMR ($CDCl_3$) 125.59 (C–NO_2), 159.16 (*C*–NHMe), 30.25 (Me–NH).

8 M.p. 94–94.5 °C, ^{1}H NMR ($CDCl_3$) 4.3 s (3H, OMe), ^{13}C NMR ($CDCl_3$) 123.10 (C–NO_2), 158.87 (*C*–OMe), 59.42 (OMe).

9 M.p. 30.5–32 °C, ^{1}H NMR ($CDCl_3$) 4.1 m (OMe), ^{13}C NMR ($CDCl_3$) 125.59 (O–N=*C*–OMe), 159.40 (N=*C*–OMe), 60.02 and 57.41 (2–OMe).

References

1 R. Calvino, A. Gasco and A. Serafino, *J. Chem. Soc., Perkin Trans. 2*, 1981, 1240.

2 H. Wieland, *J. Liebigs Ann. Chem.*, 1903, **328**, 154.

3 A. Gasco, V. Mortarini, Y. Rua and A. Serafino, *J. Heterocycl. Chem.*, 1973, **10**, 587.

4 M. A. Bianco, A. Gasco, V. Mortarini, A. Serafino and E. Menziani, *Farmaco. Ed. Sci.*, 1973, **28**, 701.

5 R. Calvino, V. Mortarini, A. Gasco, M. A. Bianco and M. L. Ricciardi, *Eur. J. Med. Chem.*, 1977, **12**, 157 (*Chem. Abstr.*, 1977, **87**, 53172k).

6 N. N. Makhova, I. V. Ovchinnikov, B. N. Khasapov and L. I. Khmel'nitskii, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1982, 646 (*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1982, 573).

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