

Oxidation of Nitrobenzofuroxans

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Summary Monoperoxosulphuric acid oxidized 4-nitrobenzofuroxan into 1,2,3-trinitrobenzene (80%) and 4,6-dinitrobenzofuroxan into 1,2,3,5-tetranitrobenzene (100%).

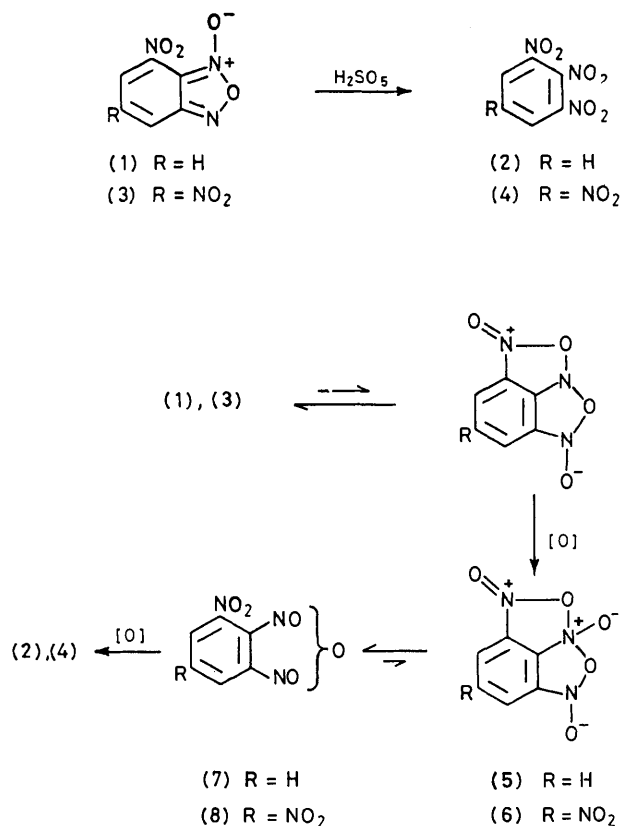
OXIDATION of 4-nitro- (1)¹ and 4,6-dinitro-benzofuroxan (3)¹ into 1,2,3-trinitrobenzene (2), m.p. 120—122 °C,² (80%) and 1,2,3,5-tetranitrobenzene (4), m.p. 129—130 °C,³ (99%) extends the only previous oxidation of a furoxan into a dinitro-compound,⁴ and in combination with the nitration

of benzofuroxan,¹ provides a preparative route to vicinal trisubstitution.

The highly efficient oxidations, † (1) → (2)[‡] and (3) → (4)⁵ were brought about by a large excess (> 50 molar) of hydrogen peroxide (90%) in sulphuric acid (98%) at 25 °C for 2 days. When polyphosphoric acid replaced sulphuric acid the yield of the tetranitrobenzene (4) was moderate (44%) but in mixtures of the two acids the yield increased with increasing sulphuric acid content and was quantitative with 80% sulphuric acid alone.

† CAUTION: 90% hydrogen peroxide is dangerous. Each reaction was repeatedly carried out on a scale (1—2 mmol) which called for less than 3 ml (140 mmol) of 90% hydrogen peroxide without mishap.

‡ Compound (2), δ (EtOAc): 8.60—8.75 (d, 2H) and 8.05—8.30 (t, 1H); *m/e* (70 ev): 213 (*M*⁺); compound (4) δ (CDCl₃): 9.3 (s); *m/e* (70 ev): 258 (*M*⁺).



SCHEME

Trifluoroperoxyacetic acid by itself or mixed with concentrated nitric acid failed to react with 4,6-dinitrobenzofuroxan but a mixture of trifluoroacetic and nitric acids and hydrogen peroxide in polyphosphoric acid transformed the furoxan (3) into the tetranitrobenzene (4) in trace amounts.

Benzofuroxan was oxidized into *o*-dinitrobenzene (20%) by both trifluoroperoxyacetic⁴ and monoperoxosulphuric acid (there was extensive degradation); however, the furoxans (1) and (3) resisted oxidation by trifluoroperoxyacetic acid and were recovered. Diminished attraction between the furoxan ring and electrophilic peroxide is the expected result of electron withdrawal into the nitro-substituent(s); however, this could be partially balanced by neighbouring group participation by the 4-nitro-substituent (see Scheme), an effect previously assumed to be operative in the degenerate rearrangement of 4-nitrobenzofuroxan and similar rearrangements.⁶ It was assumed that the oxygen atoms were introduced in separate steps. Isomerization during or after the first stage of the oxidation of the furoxans (1) or (3) into the nitroso-compounds (7) or (8) was not detected; however, we assume that a facile oxidation of a nitrosoarene into a nitroarene is one step in the reactions.

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¹ A. G. Green and F. M. Rowe, *J. Chem. Soc.*, 1913, **103**, 2023.

² L. I. Khmel'nitskii, T. S. Novikova, and S. S. Novikov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1962, 517 (*Chem. Abstr.*, 1962, **57**, 14979b), reported the oxidation of 2,6-dinitroaniline by hydrogen peroxide (96%) in trifluoroacetic acid into 1,2,3-trinitrobenzene (2), m.p. 122 °C.

³ A. T. Nielsen, R. L. Atkins, and W. P. Norris, *J. Org. Chem.*, 1979, **44**, 1181 oxidized picramide by hydrogen peroxide (98%) in sulphuric acid (100%) into the tetranitrobenzene (4), m.p. 127–129 °C.

⁴ J. H. Boyer and S. E. Ellzey, *J. Org. Chem.*, 1959, **24**, 2038. The reported procedures were adapted to the present work.

⁵ R. Nietzki and R. Dietschy, *Ber.*, 1901, **34**, 55; W. Will, *ibid.*, 1914, **47**, 704, 963. The oxidation of (3) into (4) by nitric acid reported in 1901 was refuted in 1914.

⁶ A. J. Boulton and A. R. Katritzky, *Proc. Chem. Soc.*, 1962, 257.