

## Action of Nitroalkanes on Benzofuroxan

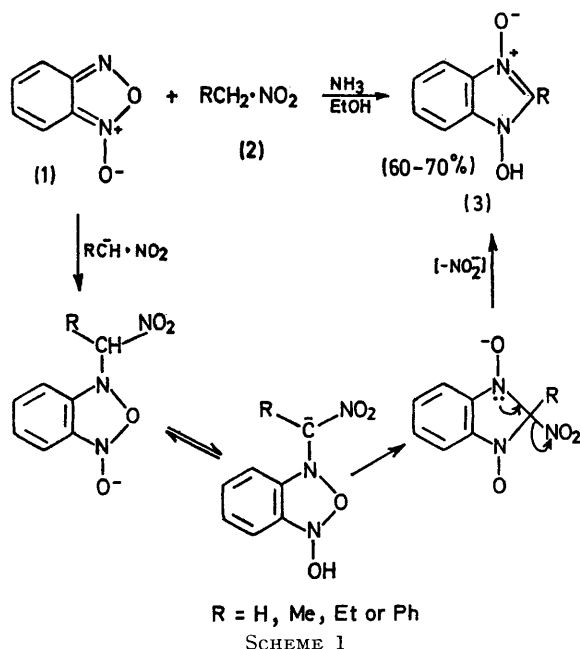
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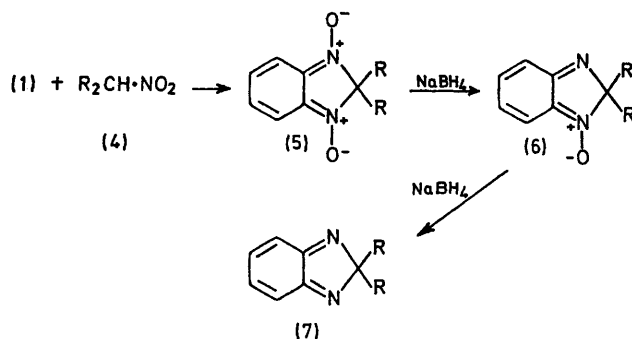
**Summary** Benzofuroxan reacts with primary nitroalkanes to give 2-substituted 1-hydroxybenzimidazole 3-oxides and with secondary nitroalkanes to yield 2,2-dialkylisobenzimidazole 1,3-dioxides.

THE synthetic usefulness of benzofuroxan (1) has been demonstrated in its reactions with 1,3-dicarbonyl compounds,<sup>1</sup> malononitrile,<sup>2</sup> enamines,<sup>3</sup> and phenols<sup>4</sup> which give quinoxaline or phenazine *N*-oxides. We now report that benzimidazole and isobenzimidazole *N*-oxides can be made by the action of nitroalkanes.

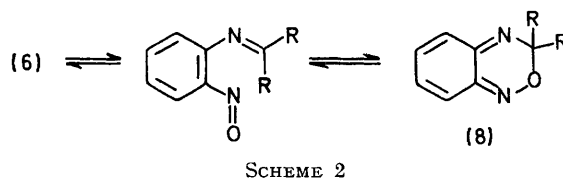
Primary nitroalkanes (2) react readily in cold ethanolic solution with benzofuroxan (1) in the presence of ethanolic ammonia (which acts both as a catalyst and as a trap for the liberated nitrous acid) to give the known<sup>5</sup> 1-hydroxybenzimidazole 3-oxides (3) in 60–70% yield. The formation of these compounds is rationalised in Scheme 1, involving initial attack of the nitroalkane carbanion at the 3-position of benzofuroxan.



With secondary nitroalkanes (4) in cold chloroform and triethylamine as catalyst, benzofuroxan reacts rapidly to give an intense red solution.† A red, crystalline product is obtained in 80–90% yield to which we assign the novel structure (5). Thus the dimethyl compound (5a), readily soluble in both water and organic solvents, shows a methyl



singlet ( $\tau$  8.28) in the n.m.r. spectrum (carbon tetrachloride) and a symmetrical AA'BB' aromatic multiplet. Similar absorptions are seen in the aromatic regions of the analogues (5b and c), all of which collapse to singlets in D<sub>2</sub>O solution. The 2,2-dimethyl compound (5a) gave acetone with hot mineral acid (but no *o*-nitroaniline), suffered reduction to *o*-phenylenediamine with hydrogen over palladium charcoal and slowly lost oxygen (1 atom equiv.) in warm, inert solvents. Removal of 1 atom equiv. of oxygen is virtually quantitative when 1 mol. equiv. of sodium borohydride in ethanol is used as the reducing agent for 30 min. The product is readily soluble in both water and organic solvents and we assign it the mono-*N*-oxide structure (6a). Its n.m.r. spectrum (deuteriochloroform) consists of a



† Commercial primary nitroalkanes give a red colour with benzofuroxan and a base owing to the presence of small amounts of secondary nitroalkanes. The sensitivity of this test is under investigation.

methyl singlet ( $\tau$  8.46) and an unsymmetrical aromatic multiplet, unchanged between  $-60$  and  $+60^\circ$ . However in  $D_2O$  solution an additional small singlet is discernible in the methyl region (*ca.* 8% of Me signal) which suggests the possibility of a valence tautomerism [(6)  $\rightleftharpoons$  (8)] involving an intermediate ring-opened structure (Scheme 2). This is reminiscent of the analogous isomerism of benzofuroxans. Reduction of this *N*-oxide with an excess of sodium borohydride in ethanol yields the isobenzimidazole (7a) in high yield. We have previously reported<sup>6</sup> the synthesis of the related cyclohexyl compound (7c) by

manganese dioxide-catalysed oxidation of its parent dihydrobenzimidazole; indeed, sodium borohydride reduction of (6c) yields the same isobenzimidazole. The dimethylisobenzimidazole (7a) showed a methyl singlet ( $\tau$  8.55) and a symmetrical AA'BB' aromatic multiplet in the n.m.r. spectrum (carbon tetrachloride).

A detailed study of the isobenzimidazoles (5)—(7) will be reported elsewhere.

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