Facile Reduction of Benzofuroxans into *ortho*-Quinone Dioximes

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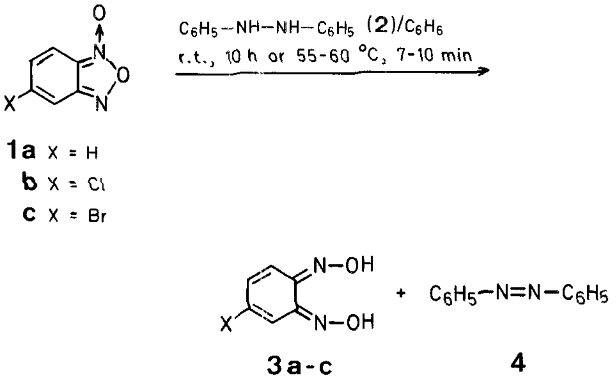
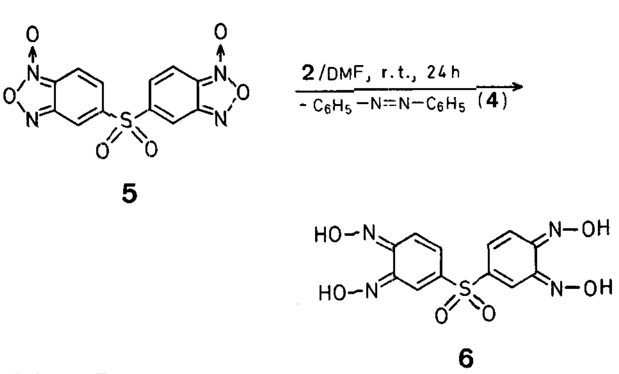
ortho-Quinone dioximes **3** are of synthetic value for the preparation of various aromatic diaza-*N*-oxides[1,2], and are useful curing agents for synthetic rubbers[3,4]. Moreover, certain metal complexes of **3**, especially those of platinum(IV), are reported to possess interesting anisotropic optical and electrical conduction properties[5,6]. The dioximes **3** are usually obtained by reducing the corresponding benzofuroxans **1** with hydrazine, hydroxylamine, related amines, thiols, sodium borohydride, or other appropriate electron-rich reagents[7]. However, reduction of **1**, using these reagents, requires controlled heating above room temperature and the desired dioxime often needs further purification.

We now report on the use of hydrazobenzene (**2**) as an efficient reducing agent for benzofuroxans **1a-c** (Scheme A). The reaction proceeds smoothly in benzene at room temperature and gives the corresponding dioximes **3a-c** in good yields. This approach is also attractive in that hydrazobenzene (**2**) is relatively cheap and is converted, during the reaction, to the valuable azobenzene (**4**) which is readily recoverable from the solvent benzene. For better yields of dioximes **3a-c**, a small excess (20%) of hydrazobenzene, and reaction times of 10-15 h are used; the employment of a larger excess (2-3 fold), and/or a longer reaction time (40 h) does not improve the yield. We also find that the reaction proceeds more quickly (7-10 min) at 55-60 °C, yet this is accompanied by a reduction in the yield.



Scheme A

As an extension of this approach, hydrazobenzene (**2**) has been successfully used for the reduction of a model bis-benzofuroxan **5** into the corresponding tetra-oxime **6** (Scheme B), and the yield is substantially higher than that we obtain using hydroxylamine. The chelating properties of **6**, and its potential to prepare new polymeric platinum complexes, are presently under study.



Scheme B

Hydrazobenzene (**2**) has rarely been used as a reducing agent for *N*-oxides. One such report[8] described the deoxygenation of pyridine 1-oxide at 140-145 °C. In the present reaction, it is postulated that the reduction proceeds as depicted in Scheme C, and involves initial hydride transfer to the receptor **1a** (or its transient *o*-dinitroso form **7**), though the possibility of stepwise electron transfer or a concerted mechanism cannot be ruled out.

o-Quinone Dioximes 3a-c:

Hydrazobenzene (**2**; Fluka, 5.5 g, 0.03 mol) is added to a solution of benzofuroxan[9] (**1a**; 3.4 g, 0.025 mol) in benzene (50 ml) and the mixture is set aside at ambient temperature. Within 4-5 h, dioxime **3a** begins to separate as shiny light brown scales, which are filtered after further 6-10 h, washed with benzene, and dried; yield: 2.3 g (67%); m.p. 151-152 °C (dec.); Lit. [10], m.p. 148-149 °C (dec.).

The reddish brown residue, left after evaporating the solvent under reduced pressure, is triturated with methanol, the precipitate collected, washed with cold methanol (to remove unchanged **1a**), air-dried, and identified as *trans*-azobenzene (m.p. 68-69 °C, undepressed upon admixture with a reference sample available from Fluka); yield: 5.0 g (92%)[11].

Under similar conditions, treatment of 5-chlorobenzofuroxan[12] (**1b**, 0.025 mol) with hydrazobenzene (0.03 mol) in benzene gives *4-chloro-1,2-quinone dioxime* (**3b**); yield: 58%; m.p. 128-129 °C,

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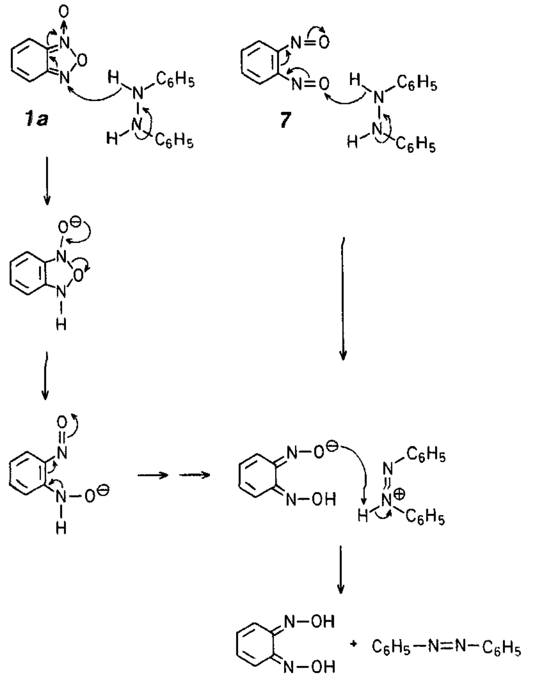

Scheme C

Lit. [13], m.p. 128 °C. Similarly, **1c**[12] gives **3c**; yield: 55%; m.p. 130–131 °C, Lit. [14], m.p. 129 °C.

In an alternative procedure a solution of **1a** (0.025 mol) and hydrazobenzene (0.03 mol) in benzene (20 ml) is heated at 55–60 °C with continuous bubbling of nitrogen. After 4–6 min, the dioxime **3a** begins to separate as a light brown solid, and the reaction is continued for a further 3–4 min. The reaction flask is then cooled, and the product filtered; yield: 60%. Similarly, the halo-benzofuroxans, **1b** and **1c**, give **3b** (yield: 48%) and **3c** (yield: 36%), respectively.

4,4′-Sulfonyl-bis-*o*-quinone Dioxime (6):

*Hydrazobenzene (**2**; 11.0 g, 0.06 mol) is added to a solution of 5,5′-*sulfonyl-bis-benzofuroxan[15] (**5**; 6.7 g, 0.02 mol) in dimethylformamide (80 ml). The reaction mixture is stirred at room temperature for 24 h and then diluted with benzene (500 ml), when the tetra-oxime **6** precipitates as fine red powder. This powder is filtered, washed with benzene, and dried; yield: 4.4 g (65%); m.p. 280 °C (dec.).

$C_{12}H_{10}N_4O_6S$	calc.	C 42.60	H 2.98	N 16.56	S 9.48
(338.3)	found	42.36	2.96	16.41	9.45

I.R. (KBr): $\nu = 3440$ (OH); 3350 (OH); 1620 (C=N); 1300 (SO_2); 1135 cm^{-1} (SO_2).

^{1}H-N.M.R. (DMSO-d_6): $\delta = 6.90$–8.50 (m, 6H); 6.10 ppm (br, 4H, OH).

In an alternative procedure a mixture of hydrazobenzene (**2**; 0.03 mol) and **5** (0.01 mol) in benzene (150 ml) is stirred at room temperature until the straw yellow colour of solid **5** disappears, with the ultimate formation of a brown solid (24 h). This solid is filtered and reacted again with hydrazobenzene (0.02 mol) in benzene to ensure complete reduction (12 h). The product **6**, thus obtained, is collected, and heated under reflux in benzene for 2–3 h, filtered, and dried; yield: 52%.

Reduction of 5 into 6 with Hydroxylamine:

Hydroxylamine hydrochloride (7.0 g, 0.1 mol) is added to a suspension of **5** (1.7 g, 0.005 mol) in water (20 ml) and the resultant mixture is warmed at 50–55 °C. Aqueous sodium hydroxide (100 ml, 10%) is then added slowly such that the temperature does not exceed 60 °C. After 15 min, the reaction mixture is filtered, the filtrate is cooled, and acidified with 6 normal hydrochloric acid whereupon **6** is obtained as a dark brown precipitate. This solid is filtered, washed with water, and dried; yield: 0.26 g (15%).

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[11] During the isolation procedure, any unreacted hydrazobenzene undergoes rapid atmospheric oxidation directly to azobenzene (**4**). This accounts for the higher recovery factor of **4** as compared to the yield of **3**.

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