Photochemical Generation of Nitric Oxide from 3,4-Bis-2'-chlorophenylfuroxan

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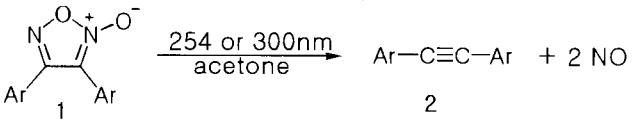
Photolysis of 3,4-*bis*-2'-chlorophenylfuroxan generated nitric oxide and bis-2-chlorophenylacetylene in 17% yield. This is the first example of the photochemical generation of the nitric oxide from the furoxan.

Nitric oxide (NO)[1] is involved in various physiological activities such as vasodilation,[2] tumoricidal and bactericidal activities,[3] and signal transduction in neurotransmission.[4] The physiological and clinical releavance of NO has led to an explosion of research into the bioactivity, detection, and generation of this molecule.[5,6] Most of the chemical sources of NO, such as *S*-nitroso or *N*-nitroso compounds, and nitroprussides, however, are not suitable for the biological application due to the instability and toxicity of these agents.[1a] We have been interested in the furoxan derivatives as potential NO-donors, and previously reported the release of NO from the 3,4-disubstituted furoxans (Furazan *N*-Oxide) through electron impact fragmentation.[7,8]

The electron impact method, however, is not suitable for the clinical application and we investigated the photochemical decomposition of furoxans. Here, we report for the first time the photolysis of 3,4-*bis*-2'-chlorophenylfuroxan **1** generating two equivalents of NO.



A solution of chlorophenylfuroxan **1** (122 mg, 0.4 mmol) in acetone (200 ml, 2.0 mM) in quartz tube was deoxygenated by argon bubbling for 30min and irradiated with 254 nm UV light in a Rayonet photochemical reactor with stirring at room temperature. After irradiation for 48h, the solution was concentrated under the reduced pressure and then subjected to the column chromatography (silica gel; 30% ethylacetate / hexane) to obtain di-2-chlorophenylacetylene **2** (17 mg, 17%) as the major product.[9] Beside the alkyne product **2**, the corresponding arylisocyanate was observed in less than 10% yield, probably due to the isomerization of the nitrile oxide as reported in the typical fragmentation of the furoxan.[10] In MeOH, the arylcyanate was converted to the carbamate as confirmed by NMR analysis. The same reaction in CH_2Cl_2 gave a similar pattern of products with less amount of acetylene **2**. The photolysis with 300 nm UV light in various solvents (acetonitrile, acetone and MeOH) also gave similar results.

This preliminary result suggests that the photolysis of 3,4-substituted furoxan derivatives is one of the efficient methods applicable in biological environments to generate NO.

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