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THE REACTION OF BENZOFUROXANS WITH BENZOFURANONES

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In previous publications we showed that benzofurazan-1-oxide (1) reacts with enamines[1,2], carbonyl compounds[2], and phenols[3] to give quinoxaline-di-N-oxides and phenazine-di-N-oxides. We now wish to report that the reaction of 1 with benzofuran-3-one (2a) in methanolic potassium hydroxide takes an unusual course giving, instead of the expected product (5, as the di-N-oxide), a yellow solid (obtained by acidification of the reaction mixture, 80% yield, m.p. 230 - 231°) whose mass spectrum shows a molecular ion at m/e 238 and a sizable M-16 peak suggestive of an N-oxide function (3a). This product dissolves in excess alkali and readily forms a monoacetate (Ac_2O-Pyridine, room temperature). Elemental analysis and the nmr spectrum (acetate of 3a: singlets at tau 1.35 and 7.8, multiplets at 1.4 and 2.4) are compatible with 3a, a formulation further corroborated by conversion of the phenolic compound into a dibromide (3b) identical with that obtained from 1 and 2b. Deoxygenation of 3a gives the known quinoxaline 4[4]. Further evidence[5] that product 3a is correctly formulated as 3[2'-hydroxyphenyl]quinoxaline-1-oxide is provided by its formation from 4 by peracid oxidation.

The reaction of 1 with benzofuran-3-ones is unusual in that the products are at an oxidation state two levels lower than expected. Evidence that benzofuranones play the dual role of substrates as well as reductants is provided by the isolation in good yield of 6 and 7[6] as by-products from the reaction of 1 with 2a and 2c respectively. As expected, the yield of 3, which is optimum when 1 and 2 are employed in a 1:2 molar ratio, falls off sharply with decreasing proportion of 2. A mechanistic interpretation will be presented in a future publication.

The phenolic mono-N-oxide products of this reaction are readily converted by refluxing acetic anhydride into the corresponding benzofuro[2,3-b]quinoxalines (3a → 5, 70%, m.p. 172 - 173°, Lit.[7] 173.5°), thereby providing a general route to a heterocyclic system for which no convenient synthetic methods are available[7,8].

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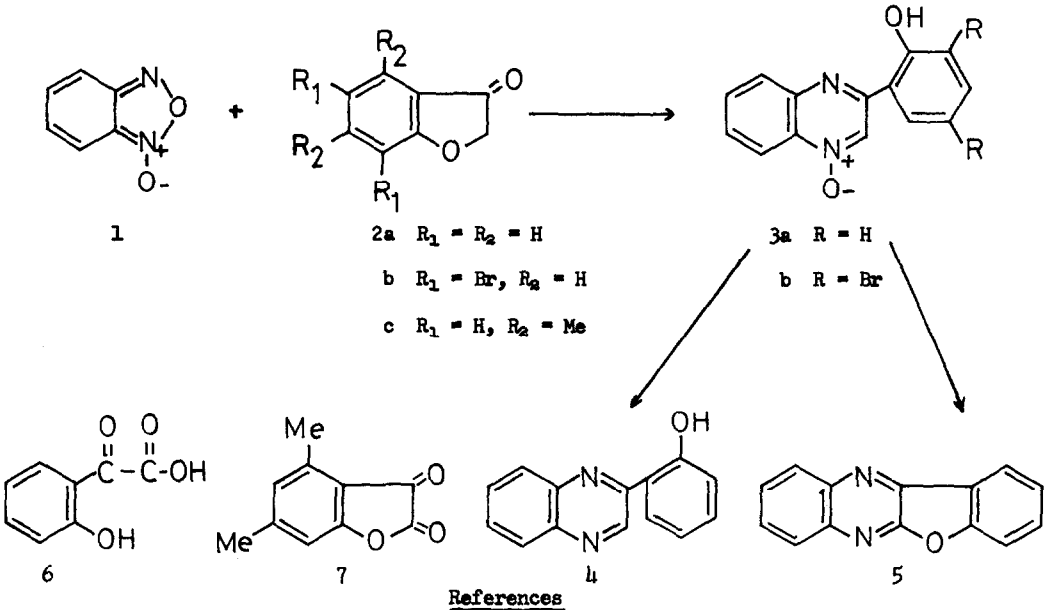

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