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A ONE-STEP SYNTHESIS OF 2-FORMYLQUINOXALINE 1,4-DIOXIDES

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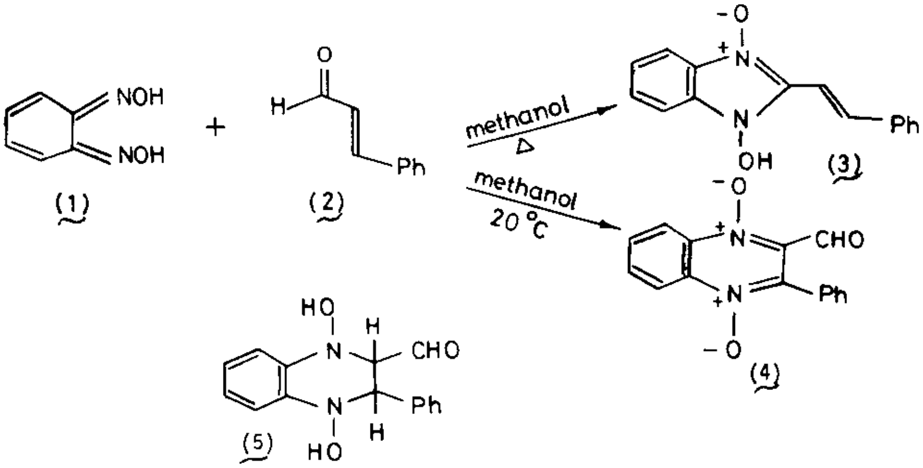
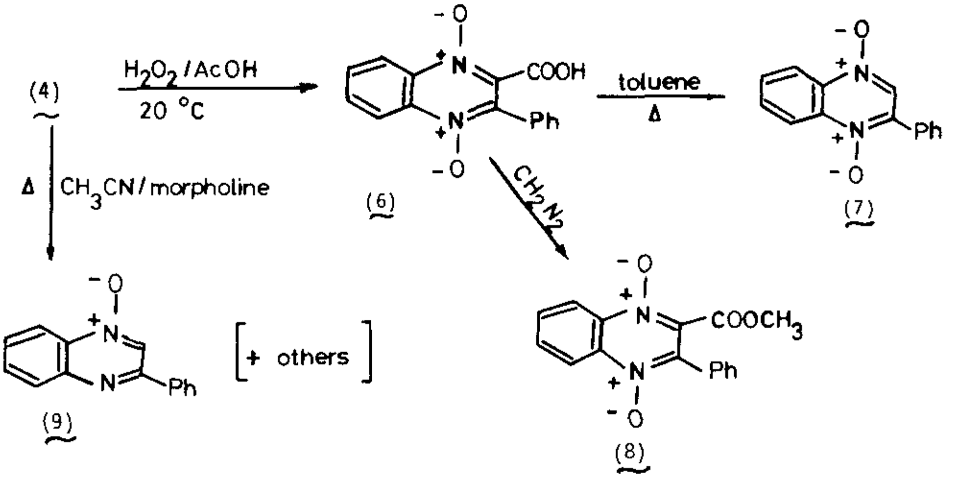
Abstract: 2-Formylquinoxaline 1,4-dioxide was easily prepared from the reaction of o-benzoquinone dioxime with cinnamaldehyde at low temperatures. A possible mechanism for the reaction is briefly discussed.

The reaction of o-benzoquinone dioxime (I) with several classes of aldehydes has been reported[1,2]. Thus, simple aldehydes gave 1-hydroxybenzimidazole 3-oxides[1], while α-ketoaldehydes led to 1-hydroxyquinoxalin-2-one 4-oxides[2], and α-hydroxy aldehydes produced quinoxaline 1,4-dioxides[2]. We wish here to report on the reaction of (I) with an α,β-unsaturated aldehyde. It was found that in refluxing methanol (I) reacts with cinnamaldehyde (2) in the manner expected of an aldehyde to yield 2-styryl-1-hydroxybenzimidazole 3-oxide (3) in 50-60% yield. If, however, the reactants are left in methanol at ambient temperature (20°C or less) they react in a different manner and produce



the hitherto unknwon 2-formyl-3-phenylquinoxaline 1,4-dioxide (4) in 35-40% yield. The structure of (4) was proved from its elemental analysis and its spectral data (ms, ir, nmr and uv). Further support for its structure was obtained from its transformation to the known[3] 2-phenylquinoxaline 1,4-dioxide (7).

The result was achieved by oxidation of (4) to give the carboxylic acid derivative (6) which upon decarboxylation produced (7). Reaction of the latter acid (6) with diazomethane afforded the methyl ester (8) which was identical with a sample obtained by an independent method involving benzofuroxan and methyl benzoylacetate (Beirut reaction)[4].



Treatment of (4) with trimethyl phosphate selectively removes the N-1-oxygen. This behaviour is to be contrasted with that of 2-formylquinoxaline 1,4-dioxide which, under the same conditions, undergoes reduction to the corresponding alcohol without any deoxygenation[5]. The behaviour of (4) under these conditions parallels that of some 2,3-disubstituted quinoxaline 1,4-dioxides[5,6]. The isolation of (4) is interesting as it was postulated that its mono-N-1-oxide is an intermediate in the reaction of benzofuroxan with (2) in refluxing benzene or acetonitrile in the presence of morpholine[7]. It was then assumed to change into the isolated product (9) by deformylation[7]. When (4) was placed under the same reaction conditions described in the literature[7], the expected (9) was isolated, besides other products.

The formation of (4) might be explained by a 1,4-addition of (1) and (2) leading to intermediate (5) which then changes rather easily to the aromatic system by atmospheric oxidation. The success of this reaction, coupled with a recently described facile reduction of benzofuroxan into (1)[8], points to a way of easy synthesis of 2-formylquinoxaline 1,4-dioxides by the employment of other α,β-unsaturated aldehydes under suitable conditions.

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