INDOLE-SINGLET OXYGEN REACTIONS. A NOVEL REARRANGEMENT OF THE PEROXIDIC INTERMEDIATES TO 2,3-DIHYDRO-1,4-BENZOXAZINES

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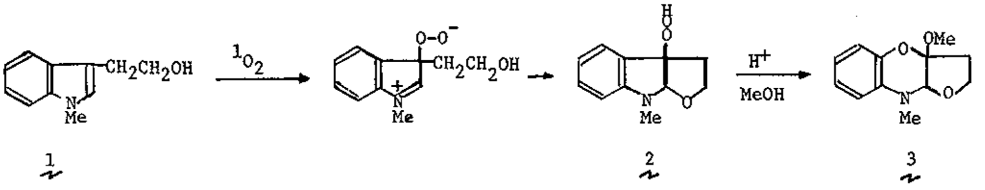
Dye-sensitized photooxygenation of various N-methylindoles has been investigated. In most cases, N-methylindoles gave the corresponding C_2-C_3 ring cleavage products which are considered to be formed through a dioxetane or an ionic peroxide such as a zwitterionic peroxide or a perepoxide. In an attempt to intercept the peroxidic intermediates by the functional group of the side chain, we have carried out the photooxygenation of N-methyltryptophol(**1**). Photooxygenation of **1** at room temperature produced the C_2-C_3 ring cleavage product, whereas at low temperature **1** gave the 3-hydroperoxyindoline **2** in 95% yield. In addition, the hydroperoxidic product **2** readily underwent a new type of rearrangement to give the corresponding 2,3-dihydro-1,4-benzoxazine **3** in the presence of catalytic amounts of acid.



Under similar conditions, photooxygenation of N-methylindole-3-propionic acid, tryptamine hydrochloride, and tryptophan methyl ester hydrochloride in methanol gave the corresponding 2,3-dihydro-1,4-benzoxazine in excellent yield. Thus the results provide a simple and general method for the oxidative transformation of indoles into 1,4-benzoxazine systems. The results also offer a suggestive information that such transformations may potentially be involved in the oxidation of indoles in biological systems. The participation of singlet oxygen in these reactions has also been demonstrated.