

## 2-(1-Methylindol-3-yl)-3-phenyldihydro-1,4-dioxin 2,3-Epidioxide, a Dioxetan resulting in Efficient Ultraviolet Chemiluminescence

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**Summary** The title dioxetan (**5**), prepared by photo-oxygenation of the dihydrodioxin (**3**) gives u.v. light ( $\lambda_{\text{max}}$  320 nm) on decomposition, the efficiency of excited singlet molecule formation being at least 50%.

THERMOLYSIS of simple, fairly stable 1,2-dioxetans gives excited carbonyl products mainly in triplet states;<sup>1</sup> quantum yields of chemiluminescence produced from them are usually very low. On the other hand, bioluminescence quantum yields are mostly very high;<sup>2</sup> excited singlet states must be predominant in the products in these cases. Although it has been suggested that bioluminescence reactions involve a dioxetan intermediate,<sup>2</sup> no dioxetan has yet been detected, probably because of their extreme instability. The high efficiency of singlet excited state production and the instability of the intermediate dioxetans in bioluminescence may be explained in terms of the conjugation of an electron-donating (such as amino-group) and

highly fluorescent chromophore with the excited state carbonyl group to be formed.<sup>3</sup> Recently both McCapra<sup>4</sup> and Schuster *et al.*<sup>5</sup> have proposed an attractive mechanism for highly efficient dioxetan decomposition of this type. The  $\beta$ -indolyl group<sup>6</sup> may be one of the best chromophores to fulfil the above requirements. We report the synthesis and properties of the title  $\beta$ -indolyldioxetan (**5**) which gives efficient u.v. chemiluminescence.

Matsumoto and Kondo<sup>7</sup> reported that the sensitized photo-oxygenation of 1-methyl-3-*trans*-styrylindole gave a 1,4-endoperoxide which is stable in aprotic solvents, but decomposes in protic solvents to 1-methylindole-3-carbaldehyde and benzaldehyde accompanied by extremely weak chemiluminescence; involvement of a transient 1,2-dioxetan was suggested. In contrast, the title dioxetan (**5**) can exist in  $\text{CDCl}_3$  at  $-46^\circ\text{C}$  and gives strong chemiluminescence above  $-40^\circ\text{C}$ . In nonpolar solvents such as *n*-hexane it gives u.v. light of wavelength 320 nm, which

corresponds to 90 kcal/mol; this is the highest energy ever observed among efficient chemiluminescent compounds. The chemiluminescence spectrum of (5) in n-hexane matches exactly the fluorescence spectrum of the diester (6) in the same solvent; the efficiencies of chemiluminescence and

excited singlet molecule formation in n-hexane were 3.6% and at least 50%, respectively.†

3-( $\alpha$ -Chlorophenylacetyl)-1-methylindole (1) was treated with  $\text{HOCH}_2\text{CH}_2\text{ONa}$  to give the hydroxyethyl ether (2) (49%), which on acid catalysed cyclization afforded the dihydrodioxin (3) (94%), white prisms, m.p. 134.5–135.5°C.‡ Photo-oxygenation of (3) in  $\text{CH}_2\text{Cl}_2$ ,<sup>8,9</sup> in the presence of polymer-bound Rose Bengal<sup>10</sup> at  $-78^\circ\text{C}$  gave an unstable compound which on warming to room temperature gave the diester (6) (74% isolable yield) with chemiluminescence. The n.m.r. spectrum in  $\text{CDCl}_3$  at  $-46^\circ\text{C}$  indicated that the first product was the 1,4-endoperoxide (4) [ $\delta$  3.02 (s, NMe), 4.10 (m,  $\text{OCH}_2\text{CH}_2\text{O}$ ) and 6.26 (s,  $-\text{NCHO}-$ )], which was easily isomerized into the 1,2-dioxetan (5) [ $\delta$  3.66 (s, NMe), 4.50 and 5.10 (m,  $\text{OCH}_2\text{CH}_2\text{O}$ ), and 7.08 (s,  $\text{NCH}=\text{C}$ )], whose disappearance on warming was directly related to the formation of the diester (6) [ $\delta$  3.72 (s, NMe), 4.61 (s,  $\text{OCH}_2\text{CH}_2\text{O}$ ), and 7.72 (s,  $\text{NCH}=\text{C}$ )] and chemiluminescence. Disappearance of the endoperoxide (4) at  $-46^\circ\text{C}$  took about 150 min to give the dioxetan (5) which was fairly stable at this temperature. A similar rearrangement of an endoperoxide to a dioxetan has previously been reported,<sup>9,11</sup> and the structures of (4) and (5) were deduced by comparison of n.m.r. data with those of analogous compounds.<sup>7-9</sup> The fluorescence of the diester (6) arises from the indole chromophore which has  $\pi-\pi^*$  character and is known to have strong electron-donating ability;<sup>6</sup> the formation of a singlet rather than a triplet excited state is preferred.<sup>3</sup> The energy level of this singlet excited state (the shortest wavelength in the fluorescence spectrum is 305 nm which corresponds to 94 kcal/mol) is lower than that of the benzoate chromophore ( $E_s$ , 102 kcal/mol;<sup>12</sup> there is no fluorescence emission at a wavelength longer than 295 nm which corresponds to 97 kcal/mol), and therefore it is reasonable to assume that the indole rather than benzoyl unit is effectively the component that is in the singlet excited state. In contrast, the 1,4-endoperoxide of 1-methyl-3-*trans*-styrylindole decomposes with weak chemiluminescence to 1-methylindole-3-carbaldehyde ( $E_s$ , ca. 84 kcal/mol) and benzaldehyde ( $E_s$ , ca. 77 kcal/mol) possibly mainly through the excited state of benzaldehyde.

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† The Hastings' standard which was used is a toluene solution of PPO, POPOP, and radioactive n-hexadecane (J. W. Hastings and G. Weber, *J. Opt. Soc. Amer.*, 1963, **53**, 1410; we thank Dr. Hastings for a standard solution). It gives quantum yields approximately twice as high as those produced using the Seliger-Lee luminol standard (J. Lee, A. S. Wesley, J. F. Ferguson, and H. H. Seliger, in 'Bioluminescence in Progress,' eds. F. H. Johnson and Y. Haneda, Princeton University Press, New Jersey, 1966, p. 35). Adam *et al.* reported a value of 1.54 for this ratio (W. Adam, G. A. Simpson, and F. Yany, *J. Phys. Chem.*, 1974, **78**, 2559).

‡ Satisfactory elemental analysis and spectral data were obtained.

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