The Chemiluminescence of a *Cypridina* Luciferin Analogue

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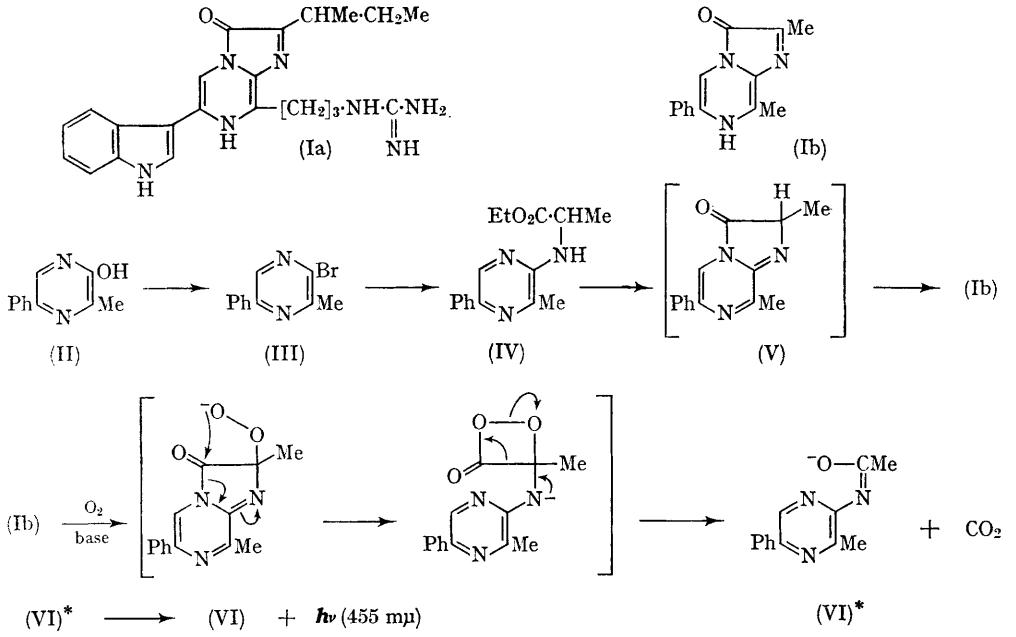
THE structure of the molecule associated with light emission in *Cypridina hilgendorfii*[1] (Ia) seemed to us to fit the pattern of chemiluminescent structures which we are studying. Evidence for a general mechanism has been obtained for the chemiluminescence of these compounds,[2] and we now suggest a probable route to bioluminescence involving this luciferin.

We have devised a convenient synthesis of a closely related compound (Ib), which is chemiluminescent, and should thus aid in the elucidation of the mechanism of the bioluminescence. 2-Hydroxy-3-methyl-5-phenylpyrazine[3] (II) was heated with PBr_3 giving (III), which afforded (IV) on condensation with alanine ethyl ester in boiling dimethyl sulphoxide. The required compound (Ib) was obtained by treatment of the ester (IV) with warm concentrated hydrochloric acid. All physical measurements (mass, u.v., i.r., and n.m.r. spectra) are in agreement with the structures given.

Oxidation of (Ib) by air in dimethyl sulphoxide in the presence of potassium t-butoxide gave (VI) as the major product (89% yield). The nature of the other very minor products will be discussed in a later publication. Strong blue light, λ_{max}



455 mμ was emitted, the spectrum of which agreed exactly with the fluorescence spectrum of (VI) in the same solution. Neither (Ib) (yellow fluorescent) nor any other product showed fluorescence in this region of the spectrum. It is interesting that the anion (VI) is the excited product, rather than the neutral amide. Using triethylamine as base in dimethyl sulphoxide, the chemiluminescence maximum still appeared at 455 mμ, but the fluorescence of the amide in this medium was entirely that of the neutral species (λ_{max} 380 mμ). Emission from the excited state obviously occurs before protonation.

Related compounds are under investigation and we are attempting to confirm that the details of the mechanism shown do indeed apply to *Cypridina* luciferin. We also hope to report shortly on a related scheme for firefly luciferin.

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