A Chemiluminescent Schiff's Base: A Possible Mechanism for *Latia* and Bacterial Bioluminescence

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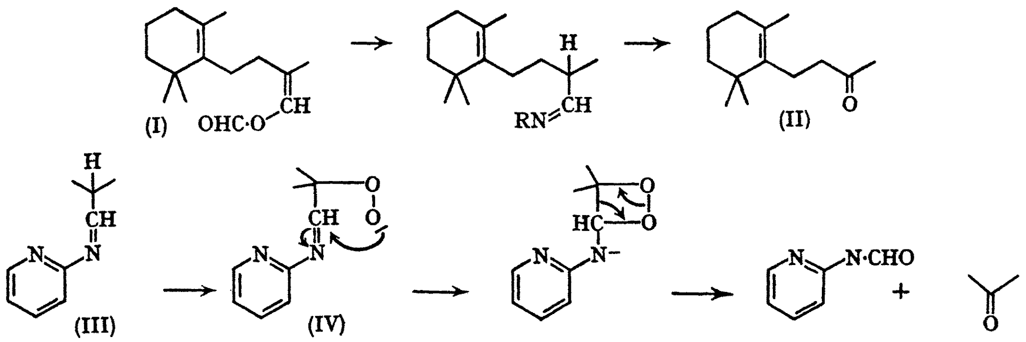
RECENT investigations of the three heterocyclic luciferins of the firefly,[1] *Cypridina*,[2] and *Renilla*[3] systems, based on the chemistry of model compounds, have produced evidence for a satisfactory general mechanism.[4] However, the application of these results to the complex and confusing bacterial luminescence,[5] and to the unexpected structure (I) of *Latia neritoides* luciferin[6] is not immediately apparent. We suggest that these systems, and perhaps others, may operate by the oxidation of a suitable Schiff's base, with the production of excited carbonyl products. Such Schiff's base formation (involving *e.g.* lysine) is known to be of wide occurrence in enzyme chemistry. Light emission can then arise in two ways. Energy transfer to an adjacent fluorescent molecule may occur, facilitated by binding on the enzyme surface, or the amino-compound (*e.g.* an amino-pyrimidine or -pteridine) may itself afford a fluorescent product. With the *Latia* luciferin, reaction with the amine could take place directly, or might involve prior formation of the required aldehyde. Isobutyraldehyde is then an exact model. In choosing 2-aminopyridine as the amine we had in mind the need to enhance the electrophilicity of the imine system in (III) and (IV). This result is usually achieved for an enzymic reaction by protonation, and such protonation is impossible in the strongly basic medium required for oxidation. Further, the expected product of the reaction, the anion of 2-formamidopyridine, is fluorescent, thus avoiding the use of a separate fluorescent acceptor.

The Schiff's base (III) was synthesised by reaction of 2-aminopyridine with isobutyraldehyde in benzene, with toluene-*p*-sulphonic acid as catalyst. Isolation of the base itself proved difficult, but its adduct with a further molecule of 2-aminopyridine was easily crystallised. Oxidation of the latter compound in Me_2SO in the presence of potassium t-butoxide, gave a strong blue light (λ_{max} 385 nm.), acetone (identified as its dinitrophenylhydrazone), and 2-formamidopyridine (80—90% yield) being the major products. It is significant that the known product in the bioluminescence of *Latia neritoides* is an analogous ketone (II). The fluorescence spectrum of 2-formamidopyridine in basic Me_2SO was identical to that of the chemiluminescence. Since luminescence in bacteria has a specific requirement for aliphatic aldehydes,[5] the observation of chemiluminescence in the Schiff's bases derived from acetaldehyde and propionaldehyde, although much weaker (particularly in the base formed from acetaldehyde) is interesting. The low level of light obtained from these aldehydes is almost certainly a result of the expected rapid polymerisation and alternative mode of oxidation of their Schiff's bases under the conditions used. We are currently studying other Schiff's bases with a view to obtaining the postulated transfer of excitation energy and enlarging the scope of this new chemiluminescent reaction.



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