The Chemiluminescence of Imidazo[1,2-*a*]pyridin-3(2*H*)-ones

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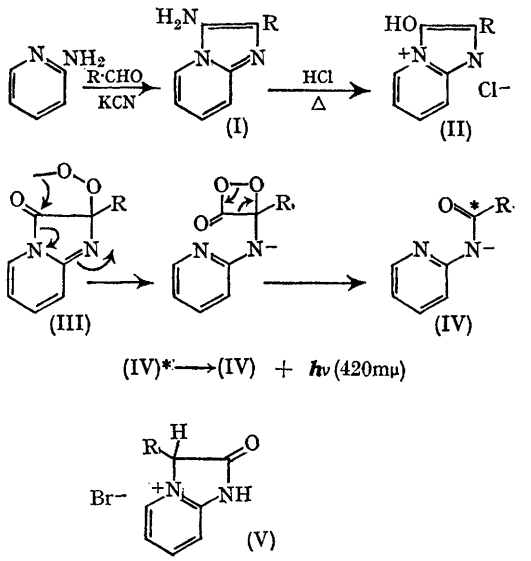
OUR earlier study[1] of the chemiluminescence of an analogue of *Cypridina* luciferin (a derivative of pyrazine) has indicated the essential features of the luminescent pathway in the natural system,[2] and it is therefore of interest to determine its generality. The simplest related structure which should be capable of reaction according to the principle outlined previously,[3] is represented by (II).†



Oxidation of (II) should form the peroxide (III), the structure of which predisposes it to an intramolecular reaction to form a four-membered cyclic peroxide (see Scheme). This result is favoured by the ready cleavage of an acyl(amino)-amidine‡ and the concomitant formation of an aromatic system. The reactive intermediate thus produced should, on decomposition, result in the excited state of a 2-acylaminopyridine or its anion. Bright blue chemiluminescence (λ_{max} 420 mμ) is observed on oxidation of (II; R = Me) in dimethyl sulphoxide using sodium methoxide as base. The major product is (IV; R = Me) (75%), and the fluorescence spectrum of the anion of this compound in dimethyl sulphoxide–base is identical with the chemiluminescence spectrum.

This ring system is most conveniently synthesised by treatment of 2-aminopyridine with the appropriate aldehyde, with subsequent addition of potassium cyanide.[4] The resulting compound (I) forms (II) by hydrolysis and cyclisation in boiling concentrated hydrochloric acid, followed by sublimation. We have found it unprofitable to isolate the intermediate carboxylic acid except in the case of (II; R = H). It may be noted that (II; R = H) is strongly yellow chemiluminescent (λ_{max} 515 mμ), a result best explained by the presence of a second acidic proton in (III; R = H) giving a yellow fluorescent anion. [The anion of (II) is also yellow fluorescent (λ_{max} 520 mμ), but when R = Me, this fluorescence is destroyed on formation of the peroxide.] Energy transfer from the excited state of (IV; R = H) to the anion of (III; R = H) then occurs. All new compounds gave satisfactory analyses and the expected mass, u.v., i.r., and n.m.r. spectra. The alternative tautomeric structures which can be written for (I), (II), and (V) are not observed.

Reaction of 2-aminopyridine with α-bromopropionyl chloride gives (V). Oxidation of this compound is not chemiluminescent, the predicted result of the lack of the features present in (II).‡ Other substituted imidazopyridines related to (II) have been prepared and are chemiluminescent.

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† This work was briefly described at the Symposium on Biologically Active Nitrogen Heterocycles, at Gregynog, Montgomeryshire, Wales, June 1968.

‡ For an interesting study of the marked difference in behaviour of acylamino- and acylimino-guanidines towards hydrolysis, see K. Matsumoto and H. Rapoport, *J. Org. Chem.*, 1968, **33**, 552.

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