

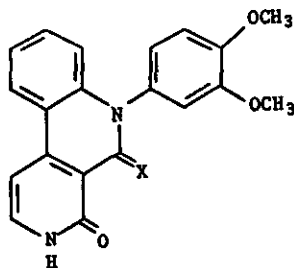
## THE SYNTHESIS OF DEHYDROPERLOLINE

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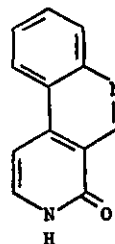
**Abstract** - Fluorenone and 3-aza-4-oxo-3,4-dihydrofluorenone react with 3,4-dimethoxyphenyllithium to form the corresponding fluorenols, which react with hydrazoic acid to form the phenanthridine. The *N*-oxides photolyse smoothly to yield dehydroperloline and its analogue as the sole product.

Perloline (1) is the major alkaloid of perennial rye grass (*Lolium perenne*)<sup>1</sup> and related species and has created some interest because of its implication in "rye grass staggers" in sheep.<sup>2,3</sup> Its structure has been determined by X-ray analysis.<sup>4</sup> Perlolidine (2), a minor alkaloid, has been synthesised by two independent groups,<sup>5,6</sup> but neither perloline, nor its oxidation product, dehydroperloline (3), have been synthesised.



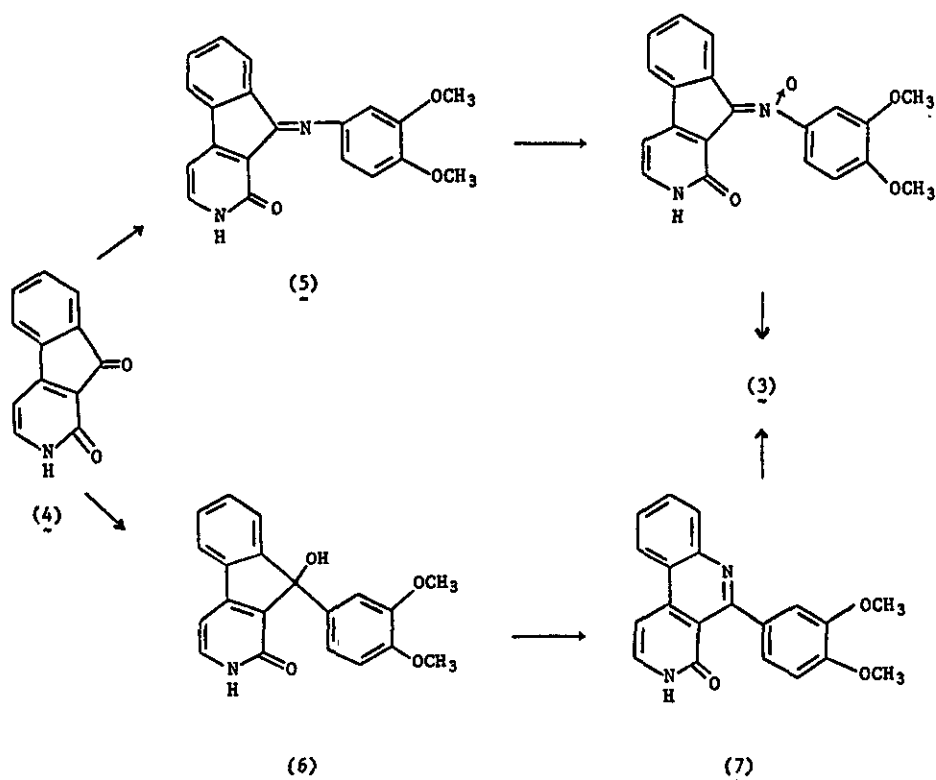
(1, X = H, OH)

(3, X = O)



(2)

Our two independent routes for the synthesis of (3) are shown below.



The two proposed routes were first tested with fluorenone as model. Reaction with 3,4-dimethoxyaniline and zinc chloride (20 min, 150°) gave the anil, m.p. 132-133°, (68%)<sup>7</sup> which was oxidised to the nitron, m.p. 212° (subl.), with *m*-chloroperbenzoic acid (72%). The nitron rearranged to the required lactam, m.p. 204-205°, on photolysis in benzene at 350 nm (92%). Reaction of fluorenone with dimethoxyphenylmagnesium bromide was unpredictable, but the reaction with 3,4-dimethoxyphenyllithium (30 min, -80°) proceeded well (71%). In contrast to 9-phenylfluoren-9-ol, which is reported to give exclusively 6-phenylphenanthridine on reaction with hydrazoic acid in chloroform,<sup>8</sup> the dimethoxyphenyl analogue, m.p. 144-145°, gave mainly the anil under these conditions. Fortunately, hydrazoic acid in polyphosphoric acid gave the required phenanthridine, m.p. 178-179°, (75%), which was converted to the *N*-oxide and photolysed<sup>9</sup> to give the phenanthridone. The former route was more satisfactory. The fluorenone (4)<sup>10</sup> formed the zinc chloride complex of the anil (5) which could not be satisfactorily decomposed, and so this pathway was not pursued. The arylfluorenol (6), m.p. 225°, prepared as above (70%) gave the phenanthridine (7), m.p. 281°, with hydrazoic acid in PPA (87%), together with a small amount of the anil (5). The corresponding *N*-oxide, m.p. 274°, (*m*-chloroperbenzoic acid, 20°, 15 h) was converted quantitatively to

dehydroperiloline (3), m.p. 285-7°, on irradiation in ethanol by sunlight for three minutes. In this case, irradiation in chloroform failed to yield (3).<sup>9</sup>

REFERENCES AND ACKNOWLEDGEMENTS<sup>12</sup>

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11. We are grateful to Dr. W.I. Taylor for spectral data that allowed confirmation of the identity of our synthetic material with (3), derived by oxidation of periloline.
12. Support of this work by the Australian Wool Board Trust is gratefully acknowledged.

Received, 14th October, 1981