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AN APPLICATION OF THE PHOTOCYCLIZATION REACTION OF SCHIFF BASES TO THE SYNTHESIS OF A PHENANTHRIDINE ALKALOID

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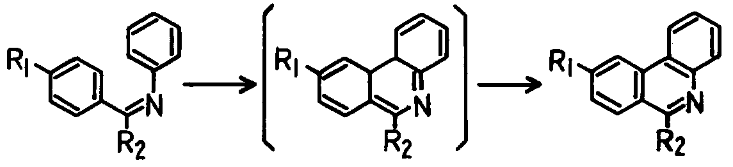
The oxidative photocyclization of the simple benzylideneaniline Ia or Ib to phenanthridine IIa or IIb was reported to proceed only in the medium of a strong acid such as sulfuric acid,[1,2] whereas the anil having a substituent with lone pair electrons Ic,[3] and the Schiff base between α-naphthylamine and α-naphthaldehyde,[4] were found to undergo the same photochemical coupling in neutral solution containing an oxidant (I_2 or O_2). These facts suggested to us that the presence of a group which interacts electronically with the benzylideneaniline system might facilitate formation of a favorable transition state even in a neutral solution to yield phenanthridines, and that successful photocyclization of methoxy- or methylenedioxy-substituted benzylideneanilines which are readily obtainable and suitable for the synthesis of Amaryllidaceae alkaloids, should be possible.

We wish to report here that the expected photochemical reaction did in fact occur in good yield and that by using this reaction we have synthesized the methobromide of ungeremine III, an alkaloid isolated from Ungernia minor.[5]

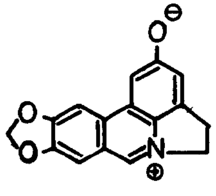


I II

a: R_1=H
R_2=H

b: R_1=H
R_2=Me

c: R_1=NMe_2
R_2=H



III

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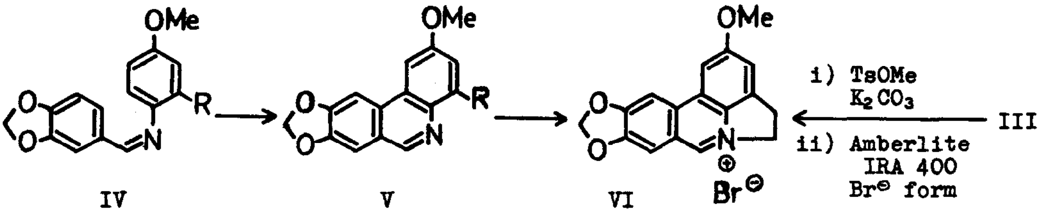
† Deceased Dec. 23, 1972

Photocyclization of IVa[6] was investigated under irradiation with a Hanovia 450 W high pressure mercury lamp in a number of solvents; n-hexane, benzene, diethyl ether, acetonitrile, and t-butyl alcohol. The best result of the transformation was observed when a diethyl ether solution of IVa was irradiated in the presence of dissolved air, giving a 55.5% yield of Va, mp 213-214°, with the 4% recovery of IVa.



IV V VI

a: $R=H$ b: $R=CH_2COOEt$ c: $R=CH_2CH_2OH$

The Schiff base IVb, mp 81.5-82.5°, prepared from piperonal and ethyl 2-amino-5-methoxyphenylacetate,[7] was analogously subjected to the photochemical reaction in ether. The cyclized product Vb, mp 144-145°, obtained in 21.4% yield was reduced with lithium aluminum hydride to Vc, mp 155-156° (55% yield), then treated with phosphorus tribromide. The resulting quaternary salt, mp 314-315°(decomp.)(82.5% yield) was shown to be identical with the methylated sample of ungeremine III, which was secured by the degradation[8] of lycorine.

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