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NOVEL PHOTOCHEMICAL REACTIONS OF ENAMINO KETONES

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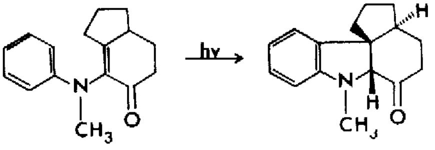
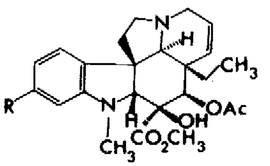
Summary: Irradiation of the conjugated N-aryl enamino ketone (V) yielded the indole (VI) resulting from a novel decomposition of the ylide intermediate.

The photocyclization of N-aryl enamino ketones has been the subject of many recent investigations [1,2,&3]. The non-oxidative photocyclization appeared to be general, resulting in the indoline ring structure. One example reported by Schultz and Chiu[2] is the photocyclization of I to yield II in 71% yield. Based upon this model study, Schultz and Chiu designed a synthetic approach to the Aspidosperma alkaloids vindorosine (III) and vindoline (IV).

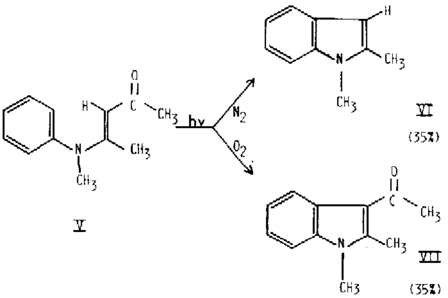


I   II

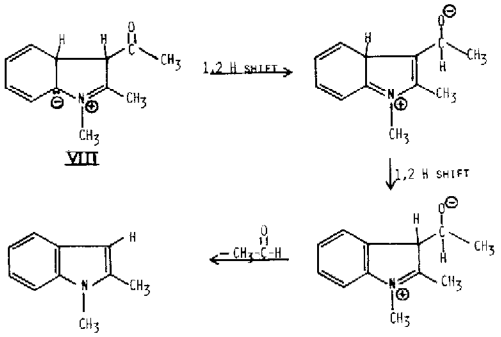


III. R = H
IV. R = OCH3

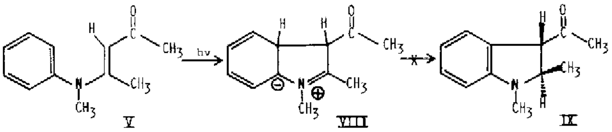
We wish now to report an apparent deviation from this non-oxidative photocyclization of N-aryl enamino ketones. Irradiation of 4-(N-methylanilino)pent-3-en-2-one (V)[4] with pyrex-filtered light (cutoff - 280nm) yielded two major products[5]. The products were separated using column chromatography[6] and identified by spectroscopic methods as 1,2-dimethylindole (VI)[7] and 3-acetyl-1,2-dimethylindole (VII)[8]. Separate irradiations were carried out in atmospheres of nitrogen and oxygen. The results are depicted below. It is the opinion of the authors that both products VI and VII are formed via the ylide intermediate VIII. Although ylide intermediates have been proposed in earlier reports[1,2,&3], the formation of the product VI with the loss



of acetaldehyde is a dramatic deviation from previously observed photocyclizations of enamino ketones. One possible mechanism for the product formation under anaerobic conditions involves two consecutive 1,2-hydride shifts, followed by the loss of acetaldehyde to form the indole VI as depicted below. Although several minor products were observed, the 2,3-dihydroindole product



IX like those reported in earlier photochemical investigations[1,2,&3] of N-aryl enamino ketones was not detected.



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References and Notes

1. K. Yamada, T. Konakahara, and H. Iida, Bull. Chem. Soc. Japan, **46**, 2504 (1973).
2. A.G. Schultz and I-Chiu, Chem. Commun., 29 (1978).
3. A.G. Schultz and W.K. Hagman, J. Org. Chem., **43**, 4231 (1978).
4. N-aryl enamino ketone V was prepared from N-methylaniline and 2,4-pentanedione by a method similar to that described by Yamada in reference 1.
5. In a typical photolysis, 600 ml of 0.004 M acetonitrile solution of V was saturated with N_2 and irradiated for 2 hr. using a Hanovia medium pressure mercury vapor lamp.
6. The photolysis mixture was eluted from alumina using carbon tetrachloride containing increasing amounts of chloroform.
7. For an nmr spectrum of 1,2-dimethylindole, see Charles J. Pouchert and John R. Campbell, "The Aldrich Library of NMR Spectra", **8**, 52 (1974).
8. W. Borsche and H. Groth, Justis Liebig Ann. Chem., **549**, 238 (1941).

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