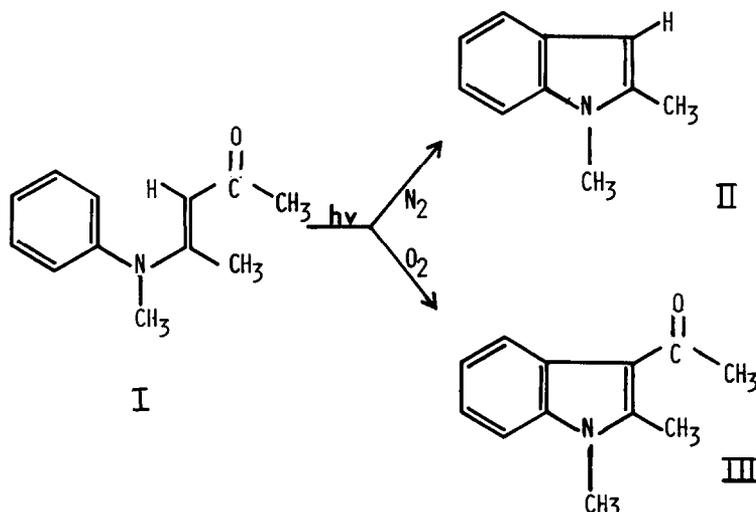


THE PHOTOCHEMISTRY OF 4-(N-METHYLANILINO)-PENT-3-EN-2-ONE

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Summary: Low conversion irradiation studies indicate that the *cis* and *trans* 3-acetyl-1,2-dimethylindolines are intermediate products in the photosynthetic production of 1,2-dimethylindole from 4-(N-methylanilino)-pent-3-en-2-one.

In an earlier paper¹ from our laboratories, it was reported that the irradiation of 4-(N-methylanilino)-pent-3-en-2-one (I) yields 1,2-dimethylindole (II) under anaerobic conditions and 3-acetyl-1,2-dimethylindole (III) under aerobic conditions.



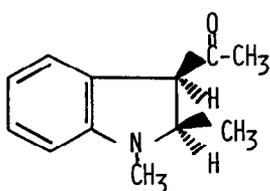
The potential utilization of this photocyclization reaction, as a pathway leading to many interesting heterocyclic compounds, demanded further investigation at low conversions into the mechanistic pathway followed in this reaction.

Varying conversion irradiation studies² of solutions of I were carried out and product distributions were carefully monitored by glc analysis³. Results from these studies at low conversions indicated that 1,2-dimethylindole was not formed directly, but instead, initial irradiation resulted in formation of two

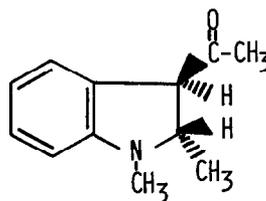
different primary photoproducts along with the expected 1,2-dimethylindole and a minor product ($\approx 10\%$), identified by gc/mass spec and nmr as 1,2-dimethylindoline.

Identification of the primary photoproducts were made on the basis of the following spectral data: Compound IV -- mass spectrum m/e (relative intensity) 189 (15.1%), 172 (14.9%), 147 (10.4%), 146 (100.0%), 131 (57.1%), 130 (21.8%); nmr ($CDCl_3, \delta$) 1.22 (d, $J=6.38$ Hz, 3H), 1.98 (s, 3H), 2.66 (s, 3H), 3.2 (m, 1H), 3.81 (d, $J=9.34$ Hz, 1H), 6.3-7.3 (m, 4H). Compound V -- mass spectrum m/e (relative intensity) 189 (19.0%), 147 (10.9%), 146 (100.0%), 132 (10.3%), 131 (61.8%), 130 (23.2%); nmr ($CDCl_3, \delta$) 1.28 (d, $J=6.15$ Hz, 3H), 2.25 (s, 3H), 2.75 (s, 3H), 3.68 (m, 2H), 6.4-7.3 (m, 4H).

On the basis of the spectral data shown above and earlier observations of similar photocyclizations^{4,5}, compound IV was identified as cis-3-acetyl-1,2-dimethylindoline and compound V as its trans isomer.



IV



V

The results of the varying conversion irradiations are depicted in Figure 1. As can be seen from the trends shown in Figure 1, compounds IV and V appear at very low conversions of starting enamino ketone I and quickly increase with time until the concentration of starting material decreases sufficiently to slow the reaction. 1,2-Dimethylindole appears in the reaction mixture only after the formation of considerable concentrations of IV and V. The concentration of 1,2-dimethylindole and 1,2-dimethylindoline continues to increase until

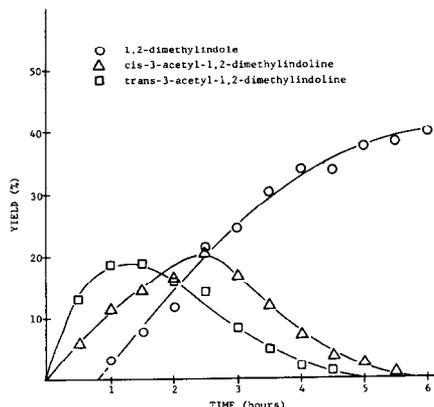


FIGURE 1. PHOTOLYSIS OF 4-(N-METHYLANTILINO)-PENT-3-EN-2-ONE

compounds IV and V are no longer present in the photolysis mixture.

The stereospecificity of similar photocyclizations is well documented^{5,6}. On the basis of these earlier reports, we propose the scheme shown below to rationalize the observation of both cis and trans photoproducts⁷.



As can be seen from the trends shown in Figure 1, the trans isomer IV undergoes photoelimination at a more rapid rate than the cis isomer V. Although several mechanisms for photoelimination of carbonyl compounds have been proposed^{8,9}, more detailed investigations will be necessary to determine the exact mechanism of this reaction.

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References and Notes

1. D. Watson and D.R. Dillin, Tetrahedron Lett., 3969 (1980).
2. In a typical photolysis, 100 ml of an ethereal solution of 0.01 M enamino ketone and 0.005 M dodecane (internal standard) were placed in a photolysis tube and sealed under argon. The sample was then irradiated using a Hanovia medium pressure mercury vapor lamp equipped with a Pyrex filter.

3. Glc analysis was carried out on a Hewlett-Packard 5700A Gas Chromatograph equipped with a flame ionization detector and electronic integrator (Model 3390A) and a column of 6' X 1/8", 10% SP2100 on 100/120 Supelcoport. The flow rate used during analysis was 47 ml/min., and the column temperature was raised from 90-250°C at a rate of 8°C per min.
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5. A.G. Schultz and I. Chiu, Chem. Commun., 29 (1978).
6. M. Riviere, N. Paillous, and A. Lattes, Bull. Soc. Chim. Fr. 1911 (1974).
7. The cis isomer of the starting material could not be isolated under the conditions of the experiment. It was assumed that this was due to the low energy barrier of rotation about the carbon-carbon double bonds in tertiary N-aryl enamino ketones (See reference 10).
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