

THE PHOTOLYSIS OF 4,6,6-TRIMETHYL-5,6-DIHYDRO-2(1H)-PYRIDONE,

A NOVEL PHOTOCHEMICAL CLEAVAGE REACTION.

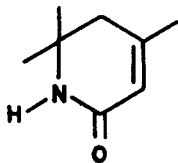
E. Cavalieri and D. Gravel

Département de Chimie, Université de Montréal,
Montréal, Québec, Canada.

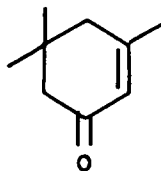
(Received in USA 11 March 1967)

Much work has been published on the photochemical reactions of α,β -unsaturated cyclic ketones. These compounds were found to undergo rearrangement, dimerization and addition reactions (1,2). It is also known that amides react photochemically to give fragmentation products among which the Norrish type I and type II fragmentations are important (3).

It therefore seemed interesting to undertake a study of the photochemical behavior of a molecule related to both types of compounds i.e. an α,β -unsaturated lactam. The substance chosen for study was the readily available 4,6,6-trimethyl-5,6-dihydro-2(1H)-pyridone (I) because of its relation to the α,β -unsaturated cyclic ketone isophorone (II) which, upon irradiation in polar solvents, yields only dimeric products (4,5,6).



I

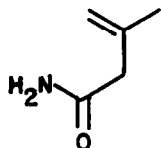


II

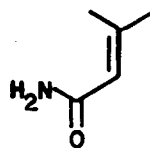
Dihydropyridone I (7) was photolyzed in dry *t*-butyl alcohol for 13.5 h. in a quartz vessel, using a Rayonet Photochemical Reactor (16 low pressure Hg lamps, 2537A). A stream of dry nitrogen was bubbled through the solution during the irradiation.

Chromatography and fractional crystallization afforded a large amount

starting material (I), a low yield of an unconjugated amide (III) and traces of a conjugated amide (IV), both having three carbon atoms less than the starting material (I).



III



IV

There was also obtained a small amount of difficultly-isolable products. Because of the apparent instability of some of these unidentified products with moisture, the photolysis of I was repeated in water. A solution of compound I was photolyzed in water using the same apparatus as described above. After 7 h., distillation of a few milliliters of the solvent permitted the isolation of acetone characterized as its 2,4-dinitrophenylhydrazone derivative, thus accounting for the loss of three carbon atoms by the starting material (I), probably via hydrolysis of an intermediate. Saturation of the remaining solution with ammonium sulfate and extraction with chloroform yielded after separation: 73% of the unconjugated amide III, 8% of the conjugated amide IV and a small percentage of unidentified compounds. No starting material was recovered from this reaction.

Compound III, m.p. 117°, mass peak 99, gave a good C,H,N, analysis. Its infrared spectrum (CHCl₃) showed characteristic bands at 3520, 3420, 1685, 1655, 1590 and 910 cm⁻¹. The n.m.r. spectrum (CDCl₃) showed peaks at δ 1.80 (3H, singlet), 2.92 (2H, singlet), 4.90 (2H, multiplet) and 5.8 p.p.m. (broad flat band). The proposed structure (III) was verified by hydrogenation of the terminal double bond to give isovaleramide identical (mixed m.p. and infrared spectra) with an authentic sample prepared from isovaleric acid.

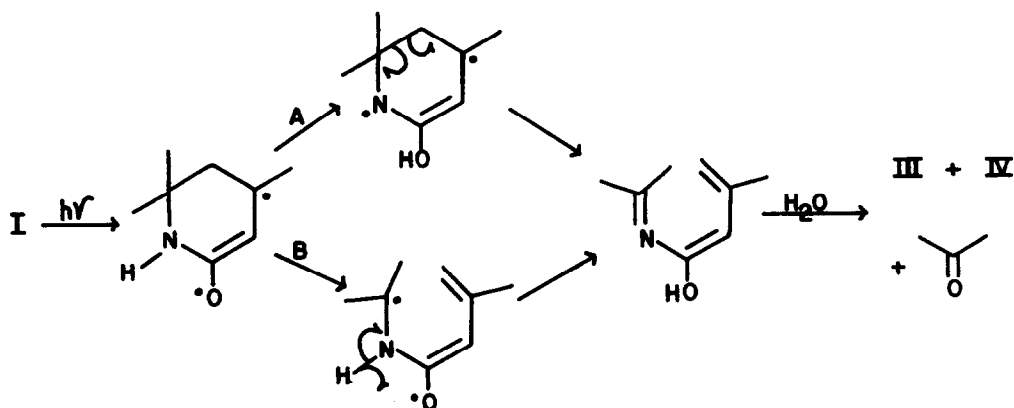
Compound IV, m.p. 108-109°, showed a mass peak of 99. Its infrared spectrum (CHCl₃) showed characteristic bands at 3520, 3420, 1685, 1645 and 1590 cm⁻¹. The n.m.r. spectrum (CDCl₃), showed peaks at δ 1.82 (3H, singlet, CH₃ trans to CONH₂), 2.11 (3H, singlet, CH₃ cis to CONH₂), 5.62 (1H, multiplet) and 6.0 p.p.m. (2H, broad band). The proposed structure (IV) was verified (mixed m.p., n.m.r. spectra and infrared spectra) by comparison with an authentic sample prepared from

3,3-dimethylacrylic acid.

The photolysis of the N-acetyl and N-methyl derivatives of I was also carried out under the same conditions. After 8.5 h. of irradiation in water, analysis by thin-layer chromatography and infrared spectroscopy did not reveal the presence of any new products. These results indicate that the hydrogen bound to nitrogen in compound I is very probably shifted in the mechanism of this photochemical reaction.

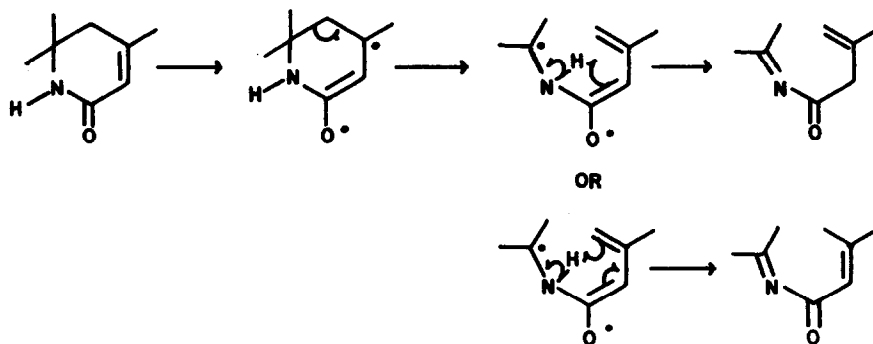
Furthermore, the irradiation of aqueous solutions of compounds III and IV showed that they are not photochemically interconvertible.

In view of these results, it appears that the observed transformations can best be rationalized with one of the following reaction paths: A or B.*



Further work is in progress to determine the exact nature of the water-labile intermediate and to examine the mechanism and scope of this new reaction.

* A referee has suggested the following alternate mechanistic path.



Acknowledgement: One of us (D.G.) is grateful to the National Research Council of Canada for providing a research grant.

REFERENCES

1. N.J. Turro, Molecular Photochemistry, p. 169 and p. 203. W.A. Benjamin, Inc., New York (1965).
2. B. Nann, D. Gravel, R. Schorta, H. Wehrli, K. Schaffner and O. Jeger, Helv. Chim. Acta, 46, 2473 (1963).
3. J.G. Calvert and J.N. Pitts, Jr., Photochemistry, p. 460. John Wiley & Sons, Inc., New York (1966).
4. E.C. Craven, Chem. Abstr., 59, 3775e (1963).
5. D.J. Trecker, A.A. Griswold and O.L. Chapman, Abstr. of Papers Presented at the 152nd Meeting, ACS, New York, Sept. 1966.
6. W. Kotlesek and D. Gravel, unpublished result.
7. H.K. Hall, Jr., J. Am. Chem. Soc., 79, 5444 (1957).