

Photochemical Rearrangement of a 1,2,4-Oxadiazoline (I)

R. M. Srivastava and Leallyn B. Clapp

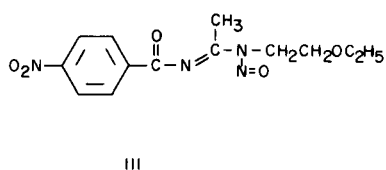
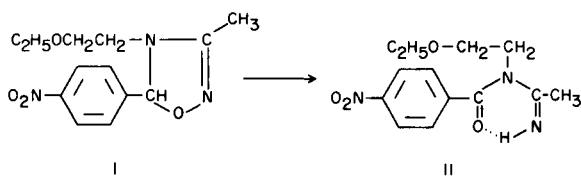
Metcalf Chemical Laboratories, Brown University

Sir:

Rearrangements of heterocyclic ring compounds under the influence of ultraviolet light have recently been reported for five-membered rings containing two double bonds: isoxazole to oxazole (2), indazole to imidazole (3), and various substituent rearrangements in thiophenes (4). In all these cases three-membered rings have been invoked as intermediates in the transformation although Wynberg and co-workers suggest that the last one may be more complicated.

In the more saturated 1,2,4-oxadiazoline ring we have found a simpler rearrangement (I \rightarrow II), also photochemically induced, which appears to involve only rupture of the weakest bond (O-N) followed by hydrogen transfer from C to N.

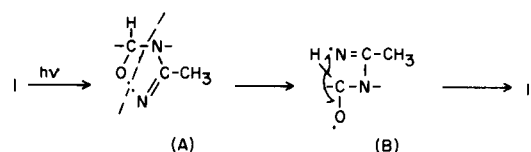
The rearrangement of 3-methyl-4-(β -ethoxy)ethyl-5-*p*-nitrophenyl-1,2,4-oxadiazoline (I) to the substituted amidine II under the influence of light was discovered in



the course of preparation and identification of a series of oxadiazolines for mass spectral studies (5). Crystallization of compound I (a viscous oil) from ethyl acetate to give II could not be repeated on fresh samples of I. This led to the discovery that the reaction was light catalyzed, black light (a source peaking at 3560 Å) being more effective

than a 150-watt bulb or a commercially lighted room.

In the mass spectral studies (5) we interpreted one of the fragmentation patterns in several oxadiazolines to be that shown by the broken line in (A). If the first bond broken in I in the less disruptive photochemical process



forms the free radical (A), then hydrogen transfer from C to N in (B) will give II.

The structure of II was deduced from NMR, UV and IR spectra and the formation of an *N*-nitroso derivative of II. The deshielded proton at C₅ in I (δ 6.16s) disappears; an upfield broad peak in II (at δ 5.63) must be due to =NH. Other NMR peaks in II follow: (deuteriochloroform, 10%) δ 1.21 (t, 3, CH₃), 2.1 (s, 3, CH₃-C=N), 3.20-3.76 (m, 6, CH₂), 8.25 (s, 4, aromatic). A strong carbonyl peak at 1735 cm⁻¹ suggests conjugation with the aromatic ring and an additional contribution from -CO-N-C=N. A doublet at 1640 and 1620 cm⁻¹ is interpreted as ν (C=N) and ν C=C (aromatic), respectively. The absorption in the UV came at λ max (methanol), 259 m μ (log ϵ 4.16), analogous to *p*-nitrobenzamide, λ max (water), 265 m μ (log ϵ 4.06) (6).

With nitrous acid compound II gave *p*-nitrobenzoic acid but nitrosyl chloride gave a 49% yield of the *N*-nitroso derivative of II (ν , =N=O, 1490 cm⁻¹) (7). A rearranged structure for the nitroso derivative, III, can be excluded on the ground that increased conjugation should give the carbonyl group a frequency lower than the 1735 cm⁻¹ absorption observed in II. In the product obtained, the carbonyl frequency was higher (1775 cm⁻¹). NMR spectrum for the *N*-nitroso derivative of II follows: (deuteriochloroform, 10%) δ 1.13 (t, 3, CH₃), 2.88 (s, 3, CH₃-C=N), 3.22-3.72 (m, 4, CH₂), 4.28 (t, 2, CH₂N), 8.33 (s, 4,

aromatic).

Whether the rearrangement described here is confined to this one oxadiazoline is under investigation.

REFERENCES

(1) Support by Public Health Service Grant CA-07521 is gratefully acknowledged. The Varian A-60A nmr spectrometer used in this research was purchased through a National Science Foundation Research Instrument Grant.

(2) B. Singh and E. F. Ullman, *J. Am. Chem. Soc.*, **89**,

6911 (1967); E. F. Ullmann and B. Singh, *ibid.*, **88**, 1844 (1966).

(3) H. Tiefenthaler, W. Dörscheln, H. Göth, and H. Schmid, *Tetrahedron Letters*, 2999 (1964).

(4) H. Wynberg, R. M. Kellogg, H. Van Driel, and G. E. Beekhuis, *J. Am. Chem. Soc.*, **89**, 3501 (1967) and earlier references cited therein.

(5) R. M. Srivastava and L. B. Clapp, *J. Heterocyclic Chem.*, **5** 61 (1968).

(6) J. T. Edward and S. C. R. Meacock, *J. Chem. Soc.*, 2000 (1957).

(7) K. Nakanishi, "Infrared Absorption Spectroscopy", Holden-Day, Inc., San Francisco, 1962, p. 50.

Received August 8, 1968

Providence, Rhodes Island 02912