

PHOTOCHROMISM IN A SERIES OF AZOMETHINIMINES BASED ON 4-PHENYL-1,2,4-
TRIAZOLINE-3,5-DIONE

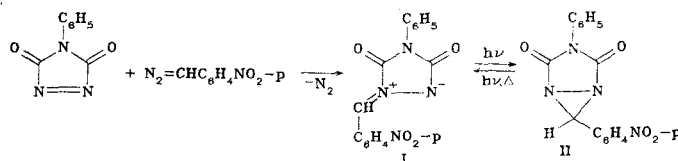
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Azomethinimines generally have a high photosensitivity. In particular, the reversible photoisomerization of pyrazolidone-3-azomethinimines to the corresponding diaziridines was observed in [1, 2].

We found that the azomethinimines from 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD) and diaryldiazomethanes do not undergo photocyclization to diaziridines when they are irradiated with a spectral filter ($\lambda > 320$ nm). Under the conditions of more severe irradiation (quartz filter, $\lambda > 210$ nm), fragmentation of the azomethinimines, the formation of dimers, and an interaction with the solvent take place [3]. The azomethinimines obtained from PTAD and monoaryldiazomethanes behave differently.

For example, when thermally stable azomethinimine I [4] in dioxane is UV-irradiated by a Hanau S-81 immersible high-pressure mercury lamp with a glass or quartz filter, photochemical isomerization to the less stable diaziridine II is observed.



The structure of a diaziridine was assigned to compound II on the basis of the determination of the molecular weight (by cryoscopy and mass spectrometry), elemental analysis, a positive reaction with an acidified starch solution of KI (which is characteristic of diaziridines), and the data from the IR and UV spectra.

Diaziridine II is converted upon irradiation or heating to azomethinimine I, as is confirmed by the appearance of a color (the azomethinimine has a yellowish orange color, and the diaziridine is colorless) and the data from IR and UV spectroscopy.

Azomethinimine I: mp 118-120°C. IR spectrum (CHCl_3): 1720, 1780 cm^{-1} (C=O). UV spectrum (CHCl_3), λ_{max} (log ϵ): 260 (4.0), 330 (3.4), 430 nm (3.7). Diaziridine II: 90% yield (following the irradiation of 0.65 mmole for 20 min), mp 152-153°C (from acetonitrile); M^+ 310. IR spectrum (CHCl_3): 1730, 1820 cm^{-1} (C=O). UV spectrum (CHCl_3), λ_{max} (log ϵ): 260 (4.1), 330 nm (2.6).

The quantum yield of the photocyclization of azomethinimine I to diaziridine II is 0.6 (in dioxane).

LITERATURE CITED

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4. L. L. Rodina, A. V. Lorkina, and I. K. Korobitsyna, *Zh. Org. Khim.*, **18**, 1986 (1982).

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