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PHOTOLYSIS OF A QUINOXALINE-DI-N-OXIDE

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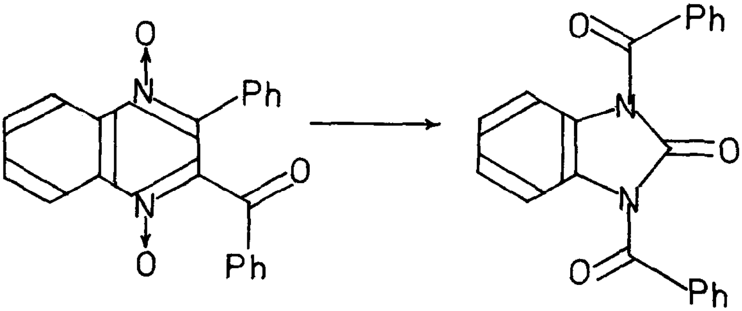
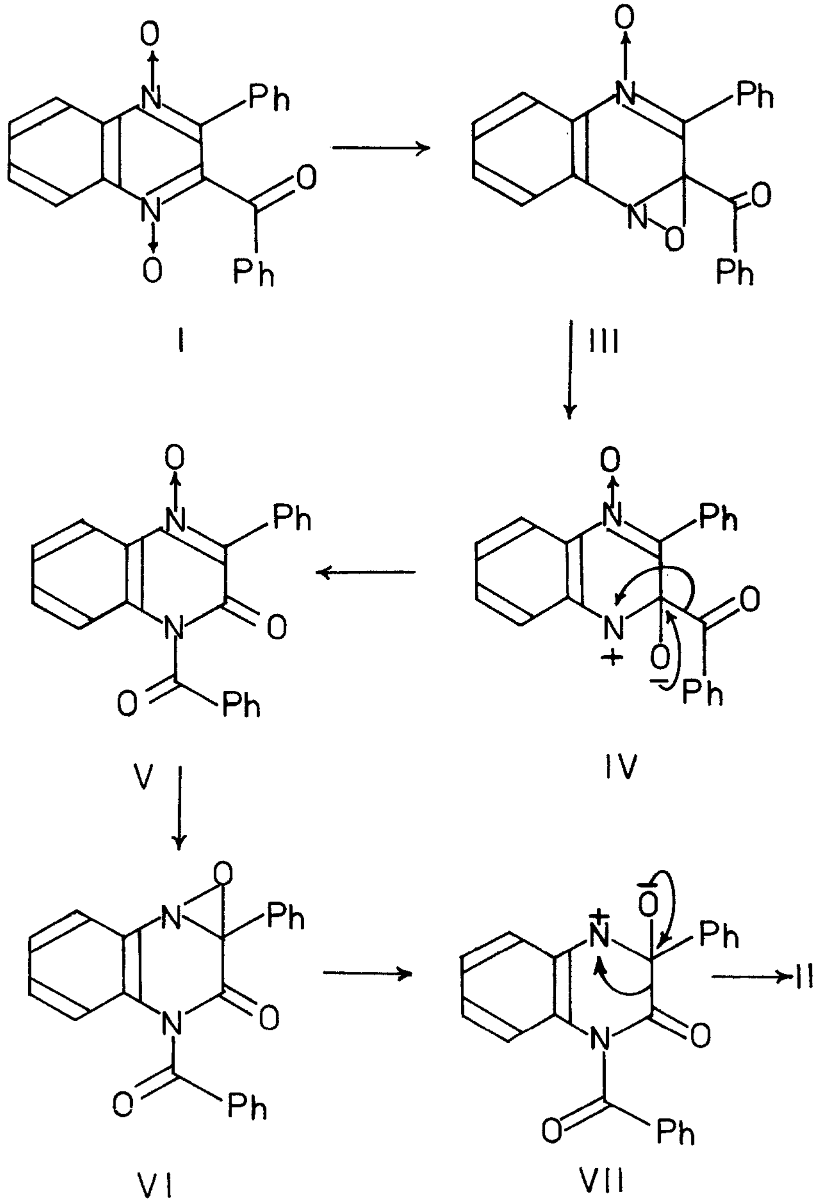
Current interest in the photochemistry of nitrones and heteroaromatic N-oxides (1) prompts us to report our findings on the photolysis of a quinoxaline-di-N-oxide derivative.

Exposure to sunlight of a methanolic solution of 2-benzoyl-3-phenylquinoxaline-di-N-oxide (2) (I) in a Pyrex flask for twelve hours, resulted in the precipitation of 1,3-dibenzoylbenzimidazolone (II) in 70% yield. Product II was identical (mixture m.p. and superimposable infrared spectrum) with an authentic sample of 1,3-dibenzoylbenzimidazolone prepared by the method of Heller (3). As expected, hydrolysis of II in base gave the known benzimidazolone and two moles of benzoic acid.



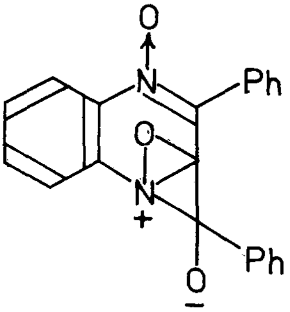
I

II


I
III
IV
V
VI
VII
II

The above rearrangement can be envisaged to involve two nitrone functions in one molecule. It is generally accepted (1,4) that irradiation of nitrones leads to oxazirane intermediates which may undergo further thermal and photochemical rearrangements. Hence, it is reasonable to assume that, on irradiation, I is transformed into the isomeric oxazirane III.

Regarding the mechanism for the formation of II from III, we favor intermediate IV arising from thermal heterolytic N-O bond fission of the oxazirane ring, as advanced by Splitter and Calvin (1d) for the thermal decomposition of 2,3-diaryloxaziranes, rather than the strained bicyclic intermediate VIII corresponding to that proposed by Padwa (5) for the photolysis of α-benzoyl-α,N-diphenylnitrone to N,N-dibenzoylaniline.



VIII

Intermediate IV, in which the positive charge on the nitrogen is delocalized by resonance with the adjacent aromatic ring, may then be postulated to undergo 1,2 benzoyl migration to the electron-deficient nitrogen giving V, the driving force for this shift being supplied by the negative charge on the oxygen. Repetition of this mechanism on the nitrone system at positions 3 and 4 would then give the observed product (II) by ring contraction (6). Further work on systems related to I is in progress.

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2 The preparation of I will be reported elsewhere.

3 Heller in *Bel*. **24**, II, 63.

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6 Another conceivable mechanism might involve initial oxazirane formation at positions 3 and 4, leading to a ring contracted intermediate. The latter rearranges to another oxazirane, which upon cleavage and benzoyl migration gives II.