

Photochemical Studies

X. On the Photolysis of 2,3-Diphenylquinoxaline *N*-Oxide to 2,4-Diphenylbenz[d]-1,3,5-oxadiazepine. An NMR Study*

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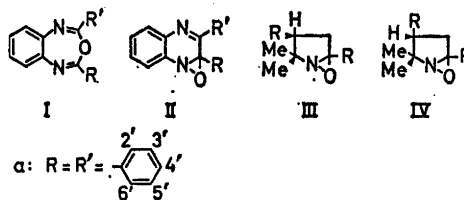
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The recent paper of Kaneko *et al.*² on the photolysis of some quinoxaline *N*-oxides to benz[d]-1,3,5-oxadiazepines (I) previously described as oxaziridines (II),³ prompts us to report some NMR measurements on the photo-product from 2,3-diphenylquinoxaline *N*-oxide, which conclusively support the symmetrical structure Ia, rather than the previously postulated oxaziridine structure IIa.

* For paper IX of this series note Ref. 1.



The 100 Mc/s ¹H resonance spectra of Ia have been examined in CDCl₃, CDCl₃-C₆D₆ (1:1) and (CH₃)₂SO solution using a Varian HA 100 spectrometer. Fig. 1 shows the 100 Mc/s ¹H spectrum of the presumed 2,4-diphenylbenz[d]-1,3,5-benzoxadiazepine (Ia) in CDCl₃ solution. From consideration of the integration and chemical shifts, the low field absorption can be assigned to the H-2' and H-6' protons. Upon strong irradiation at 746 c/s from TMS in a frequency sweep double resonance experiment, the low field absorption collapses into a sharp single absorption band (τ = 1.75 ppm) which is consistent only with the symmetrical structure Ia. If the molecule had had the oxaziridine structure IIa, the H-2' and H-6' protons in R would be shielded much more than those in R'. Bapat and St. C. Black⁴ have reported chemical shifts for phenyl protons in the 3-position of oxaziridines (III-IV) in the region 2.3-2.8 τ, whereas the low field absorption for Ia occurs at 1.7-1.8 τ. The spectra recorded in CDCl₃-C₆D₆ (1:1)

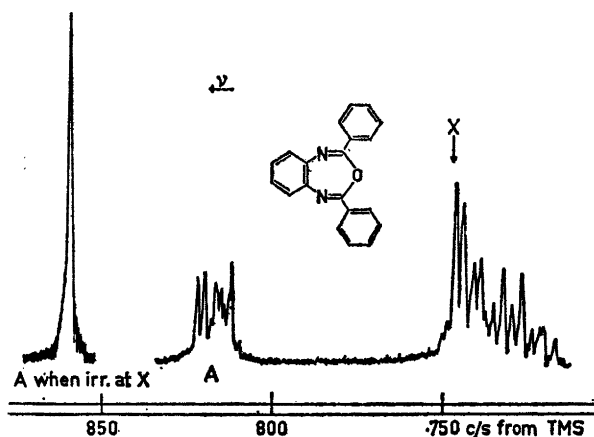


Fig. 1.

and $(\text{CH}_3)_2\text{SO}$ further confirm the structure Ia. In neither spectra is there any evidence to suggest that the low field absorption is arising from more than the AA' part of an AA'BB'C type system. Furthermore, in the spectrum recorded with CDCl_3 - C_6D_6 as solvent, a symmetrical AA'BB' type pattern can clearly be discerned which can be assigned to the protons in the benzo-group. Structure IIa would of course give rise to an ABCD type spectrum. In $(\text{CH}_3)_2\text{SO}$ solution, the benzo-group protons give rise to a single absorption band due to accidental equivalence of the four ring protons.

The present findings, together with those from UV and IR spectroscopy,²⁻³ as well as the hydrolysis experiments of Ia and related compounds,²⁻³ strongly indicate the occurrence of seven-membered rings in the photolysis of quinoxaline *N*-oxides.

By comparing this with the recent identification of benz[d]-1,3-oxazepines⁵⁻⁶ and benz[f]-1,3-oxazepines¹ formed in the photolysis of quinoline *N*-oxides and isoquinoline *N*-oxides, it can be expected that the photolysis of *N*-oxides of phthalazines and quinazolines also will result in the formation of seven-membered rings.

Apparently no stable seven-membered rings have been isolated in the photolysis of monocyclic aromatic amine *N*-oxides, but it should be noted that the products

obtained in the photolysis of several of the latter *N*-oxides indicate the occurrence of seven-membered rings as intermediates.⁷⁻⁸

Some preliminary experiments on 2,4,6-triphenylpyridine *N*-oxide have resulted only in deoxygenation by photolysis. However, further experiments are underway in the laboratory of one of the authors (O.B.).

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