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STRUCTURES OF THE STABLE PHOTO-PRODUCTS DERIVED FROM QUINOLINE 1-OXIDES AND QUINOXALINE 1-OXIDES*, **

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The recent paper$^{2)}$ of Buchardt suggesting that the stable photo-products from 2-phenylquinoline 1-oxides have the 4,5-benz-1,3-oxazepine structure (IB) rather than the oxaziridine structure (IA) prompted us to report the results of our study on this problem.

As described in our previous papers,$^{3)}$ most of the thermal and photo-chemical reactions of the irradiation products assigned to have the oxaziridine structure (IA) by us could be interpreted by assuming the formation of the corresponding oxazepines (IB) or their valence-bond tautomers (II) as the key step. Considering this fact and other chemical and spectroscopical properties (i.e., the presence of 1650-1680 cm^{-1} bands in their IR spectra and the lack of oxidizing ability), we also have some doubts on our previous assignment given to these photo-products.

While the X-ray crystallographic analysis of some of the photo-products such as Ic is in progress, a definite choice between these two possible structures could be made by the following chemical means. The first approach to this problem would be the direct comparison of the photo-products obtained from quinoxaline 1-oxides (V) having an identical substituent in their 2- and 3- position, because if the structure of the photo-products is the oxadiazepine, the same photo-products (IV) should be obtained, while if the structure is oxaziridine, different products with the same skeleton (III)

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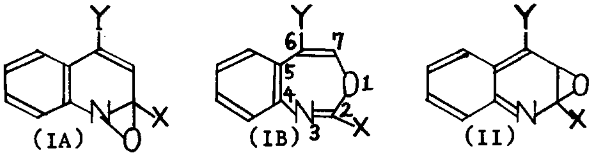
* This paper forms part IX of a series entitled to "Studies on the N-Oxides of Pi-Deficient N-Heteroaromatics". For previous paper, see Ref. 1.

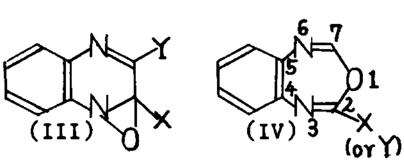
** Satisfactory microanalyses and spectral data were obtained for all the compounds, in addition to those discussed in this communication.

should be formed. The second method is the irradiation of 2,3-trimethylenequinoline 1-oxide (VIa) in an aprotic solvent, because instability of the corresponding oxazepine structure (VIIa) can be predicted from the Bredt's rule.$^{4)}$ The results of these two approaches clearly indicate that the stable photo-products obtained by the irradiation of quinoline and quinoxaline 1-oxides have the oxazepine (IB) or oxadiazepine structure (IV) and the previousl assigned oxaziridine structures (IA and III) should be discarded.



(IA) (IB) (II)

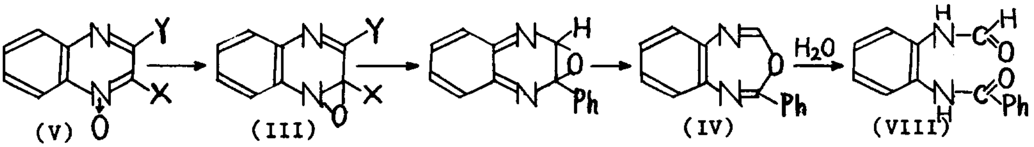
a: X = CN, Y = H
b: X = CN, Y = CH_3
c: X = CN, Y = Cl
d: X = CN, Y = OCH_3
e: X = phenyl, Y = H
f: X = CH_3, Y = H



(III) (IV)

a: X = phenyl, Y = H
b: X = H, Y = phenyl

As reported,$^{5)}$ irradiation of 2-phenylquinoxaline 1-oxide (Va) in benzene resulted in the formation of an oily material. The gas chromatography of this material showed two peaks in 7:3 ratio and the minor peak was identified as that of 2-phenylquinoxaline by comparison of its retention time with that of an authentic sample. The attempted purification of the main product by silica gel chromatography resulted in the formation of the solvolytic product, 2-formylaminobenzoylaniline (VIII). Under the same condition, 3-phenylquinoxaline 1-oxide (Vb) gave 3-phenyl-2(1H)-quinoxalinone, 2-phenylquinoxaline, and a hexane soluble photo-product in the respective yield of 20, 5, and 45% (the yield of the last compound was calculated from the yield of VIII obtained after silica gel chromatography). We postulated the following mechanism for these reactions, in which the formation of both the photo-products having the oxaziridine structure (IIIa and IIIb) and the common intermediate (IV) having



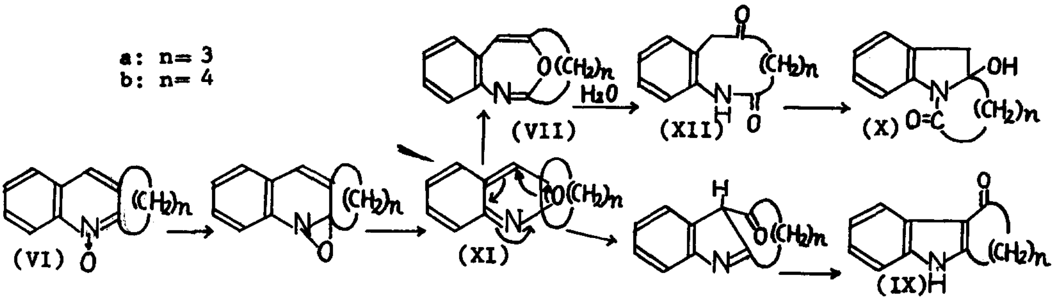
(V) (III) (IV) (VIII)

a: X = phenyl, Y = H
b: X = H, Y = phenyl

the oxadiazepine structure was assumed.5)

In our previous experiments,5) the direct comparison of these two photo-products was not made due to their high sensitivity to moisture. However, since the identification and direct comparison of these two photo-products are essential for the present purpose, we have re-examined the above experiments in order to obtain these photo-products in pure form, taking special care to avoid moisture entering into the reaction vessel in each procedure. Among the products obtained from the two irradiation reactions, the above-mentioned photo-products are the most soluble in hexane. Therefore, the portions soluble in hexane were collected by addition of hexane to the reaction mixture from both Va and from Vb. By two repetition of this procedure, almost pure desired photo-products were obtained (checked by gas chromatography). The fractions thus obtained from Va and Vb were each dissolved in a small amount of hexane and chilled by Dry Ice-acetone mixture to precipitated out the pale yellow prismatic crystals, having identical m.p. 42-46°, IR spectra [in CCl_4; 1675, 1197, 1012, 941 cm^{-1}], UV spectra [in $ClCH_2CH_2Cl$; 260, 320 mμ, logε, 4.32, 3.84], NMR spectra [in CCl_4, 3.22τ, singlet (1H), 1.8-2.9τ, multiplet (9H)], retention times in gas chromatography, and elemental analytical results ($C_{14}H_{10}ON_2$). Consequently, these experiments demonstrate without doubt that these photo-products have the 4,5-benz-1,3,6-oxadiazepine structure (IV).

From the similarity of UV, IR and NMR spectra, and chemical reactivity between IV and the photo-products (I), previously assigned to have the oxaziridine structure (IA), it seems that the 4,5-benz-1,3-oxazepine structure (IB) is also the preferred one in these compounds. To obtain a further supporting evidence for this consideration, photolysis of 2,3-trimethylenequinoline 1-oxide (VIa) was examined. Under the conditions in which 2-alkylquinoline 1-oxide are photoisomerized to I-type compounds,3c,d) anhydrous N-oxide (VIa) was irradiated in an anhydrous dichloroethane and the reaction was followed by UV spectra. After all of the N-oxide was consumed, evaporation of the solvent afforded 4-oxo-1,2,3,4-tetrahydrocarbazole6) (IXa), m.p. 220°, and 2,3-trimethylenequinoline in the respective yield of 80 and 10%. Irrespective of the temperature (0-25°) of the irradiation solution, the spectral changes during irradiation were the same and had two isosbestic points at 261 and 309 mμ, and there was no indication for the formation of I-type compounds. The mechanism of the reaction can therefore be given as in the following.



In parallel experiment, 2,3-tetramethylenequinoline 1-oxide[7)] (VIb) in benzene was irradiated under the same condition. In this case, the corresponding I-type compound was obtained and it had UV spectrum quite similar to that of the photo-product (If) obtained from quinaldine 1-oxide,[3c)] together with a small amount of tetrahydroacridine.* The purification of this crude photo-product was not possible due to its instability to moisture, reminiscent of all the I-type compounds derived from quinoline 1-oxides having an alkyl group in their 2-position.[3c,d)] Silica gel chromatography of this material resulted in the formation of Xb, m.p. 150°, IXb, m.p. 221°, and tetrahydroacridine, in the respective yield of 70, 10, and 8%. Compounds Xb and IXb show the satisfactory elemental analysis as well as the expected IR, UV and NMR spectra. For example, the UV spectra of Xb and IXb are almost identical with those of N-acetyl-2-hydroxy-2,3-dihydroindole[3d)] and 4-oxo-1,2,3,4-tetrahydrocarbazole, IXa.[6)] The experimental details of this work will be described in our full paper. Formation of the first compound is consistent with the corresponding oxazepine (VIIb),

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* The gas chromatography demonstrated that both photo-products (VIIb and If) contained small amounts (less than 10%) of the corresponding deoxygenated amines, tetrahydroacridine and quinaldine, as only one contaminant in each case.

while that of the second product seems to be expected from its valence-bond tautomer (XIb) by intramolecular rearrangement. The alternative courses for the formation of IXb may also be considered which proceed either *via* VIIb by direct rearrangement or *via* XIIb by transannular cyclization.

These experiments seem to indicate that the series of photo-products$^{3)}$ (Ia-If) prepared by us have the oxazepine structures (IBa-IBf) and support the proposal made by Buchardt.$^{2)}$

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