Hence the structure of oxypyrrolnitrin (I) was established as 3-chloro-4-(2-nitro-3-chloro-6-hydroxyphenyl)pyrrole. Examination on the possibility of artificial formation of I from pyrrolnitrin also showed such chemical oxidizing agents as oxygen and hydrogen peroxide to be useless for this transformation.

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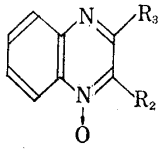
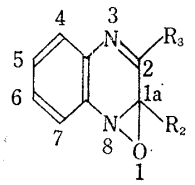
Three-membered Ring System with Two Hetero Atoms. VI.*1 Photochemical Synthesis of 1a*H*-Oxazirino[2,3-*a*]quinoxaline Derivatives and Their Thermal Reactions.

We have extended our studies on the photochemical reactions of quinoline,[1~3] isoquinoline[1,3] and pyridine N-oxides[4] to quinoxaline 1-oxides (Ia, b, c), and we now report the synthesis of two novel heterocyclic compounds, IIa and IIb, having the so far unknown 1a*H*-oxazirino[2,3-*a*]quinoxaline ring system, together with some of their thermal reactions.



I



II

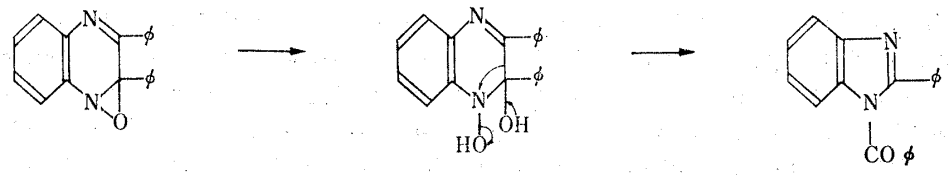
(a) $R_2=R_3=C_6H_5$
(b) $R_2=C_6H_5$, $R_3=H$
(c) $R_2=H$, $R_3=C_6H_5$

Irradiation of 2,3-diphenylquinoxaline 1-oxide (Ia)[5] in benzene was carried out as described in our previous paper.[3] After the irradiation, the irradiated mixture was concentrated under reduced pressure, and the portion soluble in hexane-ether (1:1 v/v) was chromatographed over silica gel. Only one compound, IIa, m.p. 98~99°, $C_{20}H_{14}ON_2$,*3 [UV λ_{max}^{EtOH} mμ (log ε): 262 (4.58), 326 (3.86); IR ν_{max}^{KBr} cm^{-1}: 1667s, 1330w, 1284w, 1230w, 1204m, 755m, 689m], was obtained in 60~70% yield as calculated from the N-oxide consumed. The portion insoluble in the above solvent was directly recrystallized from

*1 Part V. C. Kaneko, S. Yamada, I. Yokoe: Tetrahedron Letters, No. 39, 4701 (1966).
*2 This paper also forms part VI of "Studies on N-Oxides of π-Deficient N-Heteroaromatics," for previous paper see ref. 3).
*3 All molecular formulae indicated in this paper were supported by acceptable elemental analyses. Melting points are uncorrected.

1) M. Ishikawa, S. Yamada, C. Kaneko: This Bulletin, **13**, 747 (1965); M. Ishikawa, S. Yamada, H. Hotta, C. Kaneko: *Ibid.*, **14**, 1102 (1966).
2) C. Kaneko, S. Yamada: *Ibid.*, **14**, 555 (1966).
3) *Idem*: Rept. Res. Inst. Dental Materials, Tokyo Medico-Dental University, **2** (9), 804 (1966). See also, C. Kaneko, S. Yamada, M. Ishikawa: Tetrahedron Letters, No. 19, 2145 (1966).
4) C. Kaneko, S. Yamada, I. Yokoe, N. Hata, Y. Ubukata: Tetrahedron Letters, No. 39, 4729 (1966).
5) J.K. Landquist, G.J. Stacey: J. Chem. Soc., **1953**, 2828.

methanol and afforded the starting N-oxide*4 (Ia). The similarity of UV spectrum of IIa to those of 1a*H*-oxazirino[2,3-*a*]quinoline derivatives (III), together with its IR and NMR spectra, indicated strongly that IIa should have the corresponding oxazirane structure. Further confirmation of the structure (IIa) was provided by its facile ring contraction to 1-benzoyl-2-phenylbenzimidazole (IV), m.p. 142°, $C_{20}H_{14}ON_2$, [IR ν_{max}^{KBr} cm^{-1} : 1700] in boiling aqueous methanol. Confirmation of structure of IV was made by its conversion to 2-phenylbenzimidazole (V), m.p. 286°, $C_{13}H_{10}N_2$, by alkaline hydrolysis. The identity of the latter compound with an authentic sample[6] was assured by mixed melting point determination and superimposable IR spectra. Similar ring-contraction reactions have been found[1,2] to give indole derivatives under these conditions from III-type oxaziranes. By analogy, the mechanism shown in Chart 1 could be postulated as the most plausible one.

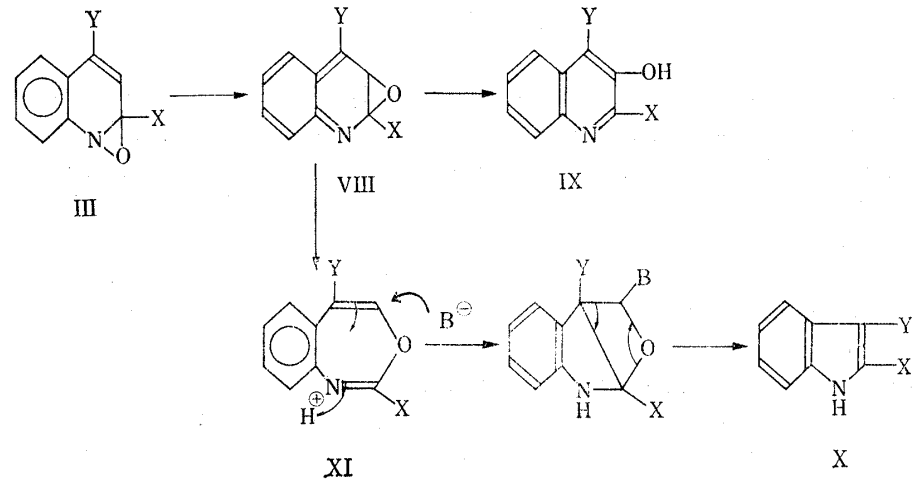


IIa IV

Chart 1.

Similarly, irradiation of Ib[6] in the same solvent as Ia and evaporation of the solvent under a reduced pressure gave rise to a neutral oil. The UV spectrum [λ_{max}^{EtOH} mμ : 254, 320] of this oil is almost identical to that of IIa and, therefore, the corresponding oxazirane structure (IIb) could be given to this compound. Differing from IIa, IIb is quite sensitive to moisture and is transformed quantitatively into the amidic compound, m.p. 154°, $C_{14}H_{12}O_2N_2$, [UV λ_{max}^{EtOH} mμ (log ε) : 230.5 (4.54); IR ν_{max}^{KBr} cm^{-1} : 3220m, 1680s, 1640s, 759s] in the course of chromatography over silica gel. The structure of this compound was confirmed to be 2-formylaminobenzoylaniline (VI) by its conversion to 2-phenylbenzimidazole in boiling dilute hydrochloric acid solution.

Finally, the irradiation of Ic[6] under similar conditions gave rise to 3-phenyl-2(1*H*)-quinoxalinone (VII),[6] m.p. 245~246°, $C_{14}H_{10}ON_2$, together with VI in respective yields of 40% and 20%. The formation of the former compound from intermediary unstable



III VIII IX

XI X

Chart 2.

*4 It seems worthy to note that the photochemical isomerization of N-oxides to the corresponding oxaziranes is much slower in quinoxaline 1-oxides than in quinoline 1-oxides.

6) E. Hayashi, C. Iijima : Yakugaku Zasshi, 82, 1093 (1962).

oxazirane (IIc) (II, R_2=H, R_3=phenyl), could be reasonably expected from the direct formation of the corresponding carbostyrils from 2-unsubstituted quinoline 1-oxides by irradiation.[1] The theoretical discussion of intrinsic unstablity and predominant carbostyril formation of 1a-H derivatives of III in their thermal decomposition will be reported shortly. The formation of VI from both IIb and IIc is very remarkable and seems to deserve a comment.

As reported already,*1 III-type oxaziranes having a cyano or phenyl group in the 1a-position tautomerize to the 2,3-epoxyquinoline derivatives (VIII), and *via* these energy-rich intermediates they give rise to either 3-hydroxyquinoline derivatives (IX) or indole derivatives (X), which may be formed from the further reactions of the valence bond tautomers (XI) as shown in Chart 2.

As VI was obtained from both IIb and IIc, the intermediary formation of 2,3-epoxyquinoxaline (XII) is very attractive. This assumption is also supported by analogy with the existence of VIII-type intermediate in the reactions of III-type oxaziranes as stated above. The valence bond tautomerization of this intermediate (XII) to seven-membered oxadiazepine (XIII) is again reasonable both from analogy to the reaction sequences shown in Chart 2, and from the theoretical consideration that the formation of the latter compound should be assisted by the formation of a stable benzenoid system in its structure. Therefore, the mechanism shown in Chart 3 can now be given to this ring-opening reaction.

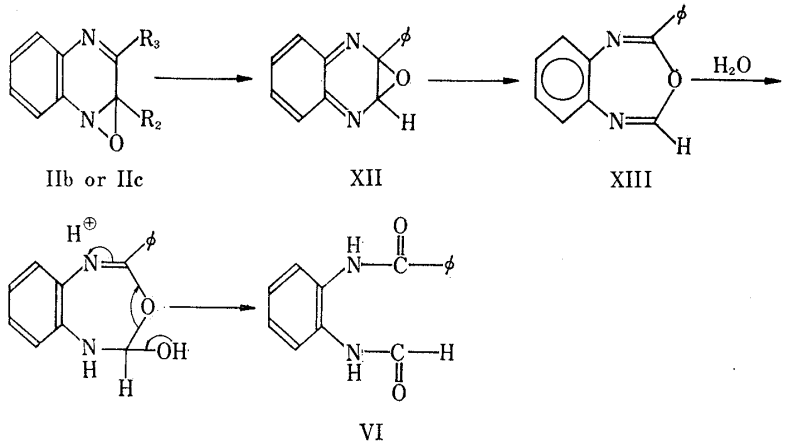


Chart 3.

The fate of oxadiazepine (XIII) is then its hydrolysis to VI as shown, since the former compound having eight π-electrons in its seven-membered ring is not aromatic and thus should behave as a Schiff's base. The attack of hydroxyl anion on C=N in XIII should be at the less-hindered carbon atom having hydrogen and not on the carbon atom bearing the phenyl group.

From this mechanism, absence of a corresponding ring-opened compound (N,N'-dibenzoyl-*o*-phenylenediamine) in the reaction products of IIa in its dark reaction*5 is also understandable, because the formation of 2,3-epoxy compound as the key intermediate should be prevented due to the steric repulsion of the two *cis*-phenyl groups.

In conclusion, the following could be said on a firm basis: Similarly to the oxaziranes derived from monoazanaphthalene N-oxides, quinoxaline 1-oxides also form the corresponding oxaziranes or their further thermal rearrangement products by irradiation. Present work enables one to conclude definitely that the photochemical alteration of

*5 So far, a variety of dark reactions has been done on II-type oxaziranes. The details will be published in our full paper.

quinoxaline 1-oxide to quinoxalinone, as reported by Landquist,[7] proceeds *via* the corresponding oxazirane (IId) (II : $R_2=R_3=H$).*[6]

The extension of this work to the N-oxides of quinazolines and phthalazines together with further work on quinoxaline 1-oxides are in progress.

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7) J. K. Landquist : J. Chem. Soc., **1953**, 2830. See also G. W. H. Cheeseman, E. S. G. Törzs : J. Chem. Soc. (C), **1966**, 157.

*6 From the analogy to nitrone-oxazirane-amide rearrangement, a similar reaction sequence has been postulated, without any definite proof. cf. for example, P. de Mayo, S.T. Reid : Quart. Rev., **15**, 416 (1961).