

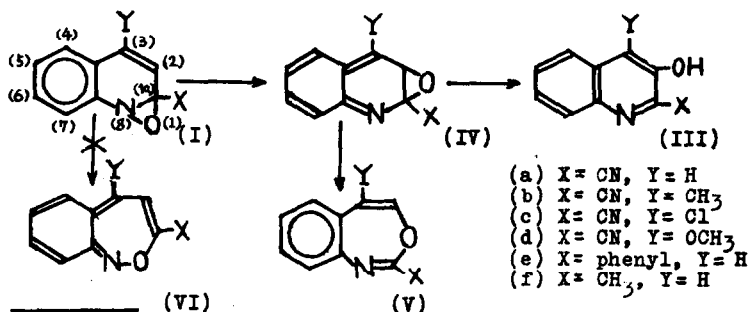
REACTIONS OF 1aH-OXAZIRINO[2,3-a]QUINOLINES AND 1aH-OXAZIRINO-  
 [2,3-a]ISOQUINOLINES VIA 7-MEMBERED OXAZEPINE INTERMEDIATES\*

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We reported previously<sup>2,3,4</sup> the photochemical isomerization of quinoline and isoquinoline N-oxides to the corresponding oxaziranes, I and II. In the course of studies on these oxaziranes, we have found that I-type oxaziranes having a cyano group in the 1a-position (Ia to Id) gave rise to the corresponding 3-hydroxyquinaldonitriles (IIIa to IIId) under quite mild conditions, and postulated a mechanism in which the formation of 2,3-epoxyquinolines (IV) was assumed as the key step.<sup>5</sup> The structure of 2,3-epoxy compounds (IV) suggests its possible valence bond tautomerization to the corresponding 7-membered oxazepines (V), since in this tautomerization



\* Three-membered Ring System with Two Hetero Atoms. V, for previous paper see ref. (1).

the latter compounds alone have the extra stability due to the benzenoid system. This extra stability is not expected for the oxazepines (VI) corresponding to I. In fact, no such valence bond tautomerization of I has as yet been observed. As the existence of IV-type compounds as intermediates has been realized, their valence bond tautomers (V) or their further decomposition products could be reasonably expected, since the former compounds (V) having 8 pi-electrons in the 7-membered ring are nonaromatic, and thus should behave as Schiff's bases. The investigation so far made on I and II has now clearly demonstrated the correctness of the above assumption, and we now report some of these reactions.

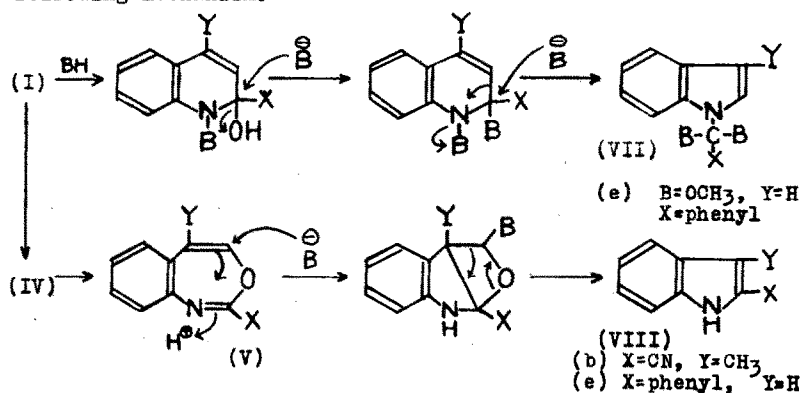
Boiling of Ie in methanol resulted in the formation of three compounds, VIIe,  $C_{17}H_{17}O_2N$ , m.p. 78-79°\*,  $\lambda_{\max}^{EtOH}$   $\mu\mu(\log \epsilon)$ ; 217.5 (4.57), 268(3.89), 289.5(3.61), and VIIIe,  $C_{14}H_{11}N$ , m.p. 186-187°, and IX,\*\*  $C_{15}H_{11}ON$ , m.p. 250°, in the respective yields of 43, 11.5, and 28%. The structure of VIIe was deduced to be N-dimethoxyphenylmethyl-indole from its nmr spectrum\*\*\* ( $CCl_4$ ; 2.44 $\tau$ (1H, d, J=3), 2.57-3.3 $\tau$ (9H, m), 5.67 $\tau$ (1H, d, J=3), 6.96 $\tau$ (6H, s)). The spectroscopic data suggested the possible structure of VIIIe to be 2-phenylindole, and this was confirmed by direct comparison with an authentic sample.<sup>6</sup> The fact that the phenyl group in the 1a-position in Ie is now attached to 2-

\* All molecular formulae indicated in this paper were supported by acceptable elemental analyses. Melting points are uncorrected.

\*\* Structure of IX is now under investigation.

\*\*\* Spectra were recorded with tetramethylsilane as internal standard. Coupling constants are in cps. The letters, s, d, m, t, designate singlet, doublet, multiplet, and triplet.

position of indole in VIIIe is very remarkable, and suggests that the mechanism is entirely different from the one\* for the formation of VII-type compounds. We therefore propose the following mechanism.



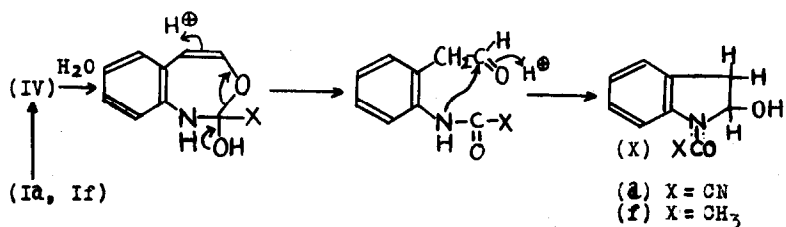
As the oxygen atom in the three membered ring in I has a lone pair of electrons, the isomerization (possibly synchronous) from I to IV is possible in both ground and excited states.<sup>7</sup>

The quantitative transformation of Ib to 2-cyanoskatole (VIIIb) induced by 2537 Å irradiation in methanol, therefore, probably proceeds in a similar manner.<sup>2</sup> An essentially similar mechanism could be given to two other reactions of I-type oxaziranes.

The first of these is the formation of N-cyanofornyl-2-hydroxy-2,3-dihydroindole (Xa), C<sub>10</sub>H<sub>8</sub>O<sub>2</sub>N<sub>2</sub>, m.p. 179-180° (dec.),  $\lambda_{\text{max}}^{\text{EtOH}}$  m $\mu$ (log  $\xi$ ); 238(4.20),  $\nu_{\text{max}}^{\text{KBr}}$  cm<sup>-1</sup>; 3400, 3240, 1700, from Ia in dilute sulfuric acid solution. The confirmation of the structure of Xa was made from both nmr spectrum (CF<sub>3</sub>COOH) showing three sets of signals at 2.6-2.9  $\tau$  (4H, m), 4.35  $\tau$  (1H, t, J=10), and 6.39  $\tau$  (2H, d, J=10) and its facile transformation to indole

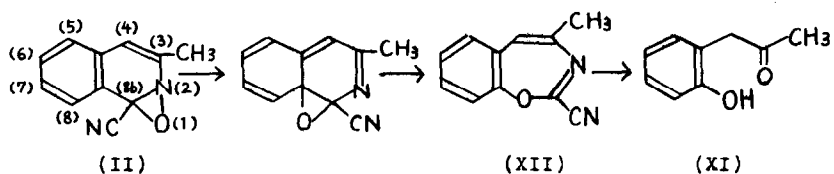
\* The mechanism implied in the formation of VII-type compounds has been reported in detail, see reference (1).

by the action of alkali. The second example is the formation of N-acetyl-2-hydroxy-2,3-dihydroindole (Xf) from If. As reported previously,<sup>5</sup> irradiation of quinaldine 1-oxide in benzene solution gave rise to the corresponding oxazirane (If), which was very sensitive to moisture, and which during the chromatography over silica gel changed to Xf, \*  $C_{10}H_{11}O_2N$ , m.p. 155-157°,  $\lambda_{max}^{EtOH}$   $\mu\mu(\log \epsilon)$ ; 247.5(4.23),  $\nu_{max}^{KBr}$   $cm^{-1}$ ; 3360, 1640, in quantitative yield. Its facile transformation to acetylindole (in  $CF_3COOH$ , the nmr spectrum of Xf is the same as that of N-acetylindole in the same solvent) and the similarity of its uv and nmr (in dimethylsulfoxide) spectra with those of Xa proved the correctness of the assigned structure. Formation of Xa and Xf could be formulated as in the following.



Finally, boiling of an aqueous methanol solution of II<sup>3,4</sup> (derived from 1-cyano-3-methylisoquinoline 2-oxide) gave rise to 2-hydroxyphenyl-2-propanone (XI),<sup>9</sup>  $C_9H_{10}O_2$ , m.p. 63.5-64.5°, in quantitative yield. By analogy, the reaction mechanism shown below could be postulated. Once again, the intermediate oxazepine (XII) is not aromatic and undergoes further decomposition.

\* Buchardt et al. reported very recently the formation of Xf by irradiation of benzene solution of quinaldine 1-oxide dihydrate, though in their paper, the mechanism implied was not given. See ref. (8).



More detailed studies on these novel heterocyclic compounds are in progress and the results will be reported shortly.

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