The reversal way of structural correlation was performed *via* cyanonornobilonine (VII), which was derived from nobilonine by the reaction with cyanogen bromide as colorless needles; m.p. 120~121°. *Anal.* Calcd. for $C_{17}H_{24}O_3N_2$: C, 67.08; H, 7.93. Found : C, 67.10; H, 8.01. mol. wt. (mass spec.) 304.[*8] ORD $[\alpha]^{13.5°}_{MeOH}$ mμ : 240 (2300), 260 (900), 275 (600), 320 (240), 338 (70; min.), 352 (90; max.). 400 (70), 600 (30). IR ν^{KBr}_{max} cm^{-1} : 2203 (vs, N-CN), 1795 (vs, γ-lactone), 1712 (vs, six membered ring ketone). NMR τ_{CDCl_3} : 9.13 (3H, d, J=6 c.p.s.), 9.01 (3H, d, J=6 c.p.s.), 8.63 (3H, s), 7.20 (3H, s), 5.60 (1H, d, J=6 c.p.s.). Nobilonine was regenerated by the reduction of cyanonornobilonine at a lower temperature (70°, 5 hr., PtO_2, H_2 65 kg./cm^2 in MeOH-AcOH).

When the reduction was carried out in a more vigorous condition (~200°, 1.5 hr.), dendrobine was obtained and the identity was confirmed by the mixed melting point determination and also infrared spectrum comparison.

Thus, in conclusion, the structure of nobilonine is proved to be shown by the formula (II), and its absolute configulation is identical to that of dendrobine.[6]

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Photochemical Rearrangement of Quinaldine 1-Oxide

Chemistry of the N-oxides of aromatic N-heterocycles has been studied extensively but most of the investigations have been directed to their ionic reactions. In spite of the rapidly expanding knowledge of photochemistry, photochemical reactions on these compounds have not yet been exploited to any great extent. That prompted us to investigate this type of reaction in this field, particularly, with pyridine and quinoline 1-oxides and their derivatives, and the present communication deals with the photochemical rearrangement reactions in the aromatic N-oxide system.

On ultraviolet irradiation[1] of quinoline 1-oxide in an ethanolic solution at room temperature, carbostyril was obtained in 60~70% yield, together with a minor amount

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1) 100 W mercury high-pressure arcs (Osawa Denki Co.) was used as a light source throughout the following experiments.

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(ca. 5%) of a deoxygenated product, quinoline.[2] A similar and undoubtedly related photochemical rearrangement of N-oxide of the aromatic system has its precedent in the literature. Landquist[3] converted quinoxaline N-oxide to 2-quinoxalinol and Kosuge, *et al.*[4] observed the formation of a simply deoxygenated product, 4-nitroquinoline, as a minor but only detectable product from the corresponding N-oxide by irradiation.

To investigate the scope of the photochemical rearrangement of quinoline 1-oxide, a number of N-oxides have been examined. While under similar reaction conditions isoquinoline 2-oxide gave isocarbostyril (30%) and isoquinoline (20%) as expected, pyridine 1-oxide was resistant to the reaction and no compounds were identified except the starting material.

On the other hand, we have found that quinaldine 1-oxide underwent a fascinating rearrangement reaction. On irradiation of ultraviolet rays in a methanolic solution, quinaldine 1-oxide gave two crystalline compounds, I, m.p. 233~234°, UV $\lambda_{\max}^{\mathrm{EtOH}}$ mμ: 271, 326, II, m.p. 75~76.5°, UV $\lambda_{\max}^{\mathrm{EtOH}}$ mμ: 272, 280, 331 and an oily substance, III, melting point of the picrate, 98~99°, UV $\lambda_{\max}^{\mathrm{EtOH}}$ mμ: 240, 291.5, 300, in yield of 22, 16, and 8%, respectively, together with a very small amount of quinaldine. 2(1*H*)-Quinolone structure of I and II was anticipated by the presence of carbonyl bands at 1645 cm^{-1} in I and 1650 cm^{-1} in II and similarity of their ultraviolet spectra with that of carbostyril. Actually, I and II were demonstrated as 3-methylcarbostyril and 1-methylcarbostyril, respectively, by a mixed melting point determination with authentic samples prepared by the settled synthetic routes.[5,6] No reaction of III with ketonic reagents, together with the spectral evidences and its elemental analysis, combined with the formation of indole through hydrolysis, pointed (III) might be 1-acetylindole. The structure of (III) was

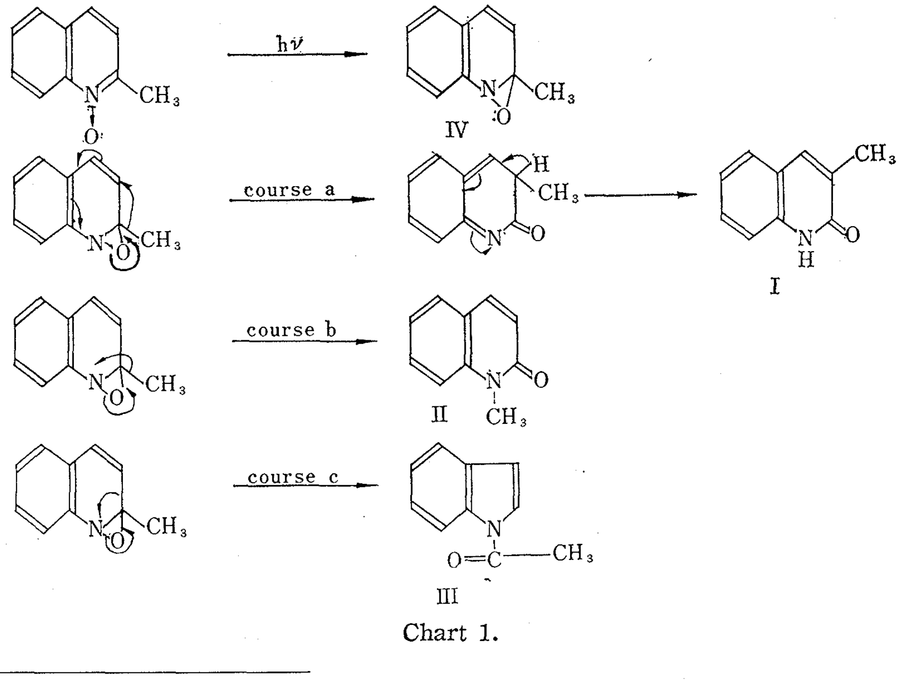

Chart 1.

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[2] While preparing this manuscript, we found that the photochemical rearrangement of quinoline 1-oxide to carbostyril in an aqueous solution had been reported by O. Buchardt (Acta. Chem. Scand., **17**, 1461 (1963)).

[3] J. K. Landquist: J. Chem. Soc., **1953**, 2830.

[4] T. Kosuge, K. Adachi, *et al.*: Yakugaku Zasshi, **85**, 66 (1965).

[5] 3-Methylcarbostyril was prepared through 3-methylquinoline 1-oxide by the method described by E. Ochiai and T. Yokokawa, Yakugaku Zasshi, **75**, 213 (1955).

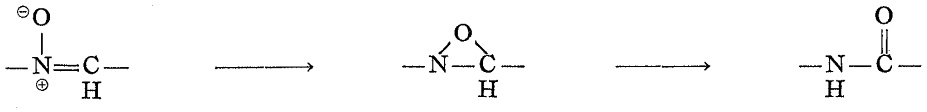
[6] 1-Methylcarbostyril was obtained by methylation of carbostyril according to the procedure of C. Rath, Ann., **489**, 107 (1931).

confirmed by a mixed melting point determination of its picrate with that of authentic 1-acetylindole.[7)]

Thus, the reaction of quinaldine 1-oxide represents a novel type of photochemical rearrangement, that is, rearrangement of the oxygen of the aromatic N-oxide group accompanied by concomitant rearrangement of the alkyl group attached to the carbon atom to which the oxygen was to be rearranged. The mechanism shown in Chart 1 for the novel photochemical transformation could be postulated.

The three-membered intermediate (Ⅳ) formed by internal addition collapses to the final products (I) and (Ⅱ) with the synchronous rearrangement of the methyl group to the neighboring atoms, that is, either to C-3 (course a) or to the nitrogen atom (course b). The same intermediate could also explain the formation of Ⅲ through the migration of C_2-C_3 bond, instead of methyl group, as illustrated in course c in the above chart.

Plausibility of the formation of the three-membered intermediate (Ⅳ) is supported also by the following facts : (i) In a nitrone system (V), a three-membered oxazirans (Ⅵ) formed by irradiation are supported to be the intermediate of the reaction.[8)] Usually, oxaziran compounds are too unstable to be isolated, because of the spontaneous rearrangement to amides (Ⅶ) but in some cases, the oxazirans were actually isolated.[9)]



V Ⅵ Ⅶ

(ii) No 4(1*H*)-quinolone derivatives had been detected in the irradiated reaction mixtures of quinoline and quinaldine 1-oxide. (iii) Insensibility of pyridine 1-oxide to this reaction could be due to the greater delocalized character of the double bond between N_1 and C_2 in the compound, compared to those of azanaphthalene N-oxides. Therefore, the activation energy to the oxaziran type intermediate, should be much larger in the former than in the latter.

Investigation for the scope and further clarification of the mechanism of the rearrangement is now under way in our laboratory.

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[9)] *a*) W. D. Emmons : J. Am. Chem. Soc., **79**, 5739 (1957). *b*) R. Bonnett, V. M. Clark, A. Todd : J. Chem. Soc., **1959**, 2102. The fact that irradiation of 2-substituted Δ^1-pyrrolidine 1-oxide failed to yield oxazirans was reported in this reference.