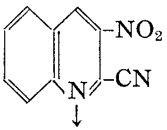
UDC 547.831.7.07

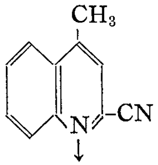
The Formation of 2-Cyanoquinoline 1-Oxide Derivatives by the Nitration of Quinaldine 1-Oxide Series with Acyl Nitrates

In a previous paper, Ochiai and Tanida[1] obtained yellowish brown crystals (I), $(C_{10}H_5O_3N_3)_n$, m.p. 249~250°, as a by-product of 3-nitroquinaldine 1-oxide and quinoline-2-methanol benzoate, when quinaldine 1-oxide was treated with an excess of benzoyl nitrate. Later, Tanida[2] obtained a small quantity of yellow needles (II), $(C_{11}H_8ON_2)_n$, m.p. 185~187°, by the reaction of 2,4-dimethylquinoline 1-oxide with benzoyl nitrate. At that time it was presumed that these compounds are glyoxime peroxide (furoxan) derivatives (IV). When quinaldine 1-oxide was treated with acetyl chloride and silver nitrate at the boiling point of chloroform, a similar product (III), $(C_{10}H_6ON_2)_n$, m.p. 170.5~171°, was obtained again together with quinoline-2-methanol acetate. In the present study, the structure of these compounds was reinvestigated.

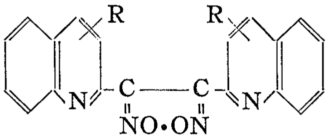
Infrared spectral curve of (III) exhibited a characteristic peak at 2252 cm^{-1} which might be assigned to a cyano group. According to Kubota's rule,[3] it was considered that (III) had an N-oxide group, because its ultraviolet absorption spectrum showed a remarkable solvent effect. Moreover, the molecular weight measurement by the Rast method was consistent with the monomolecular composition, $C_{10}H_6ON_2$. On the basis of these data, it seemed most reasonable to assume that (III) is 2-cyanoquinoline 1-oxide and it was actually identified by admixture with an authentic sample prepared through Daeniker's route.[4] By a similar method to that employed in the case of (III), (II) was also determined to be 2-cyano-4-methylquinoline 1-oxide.



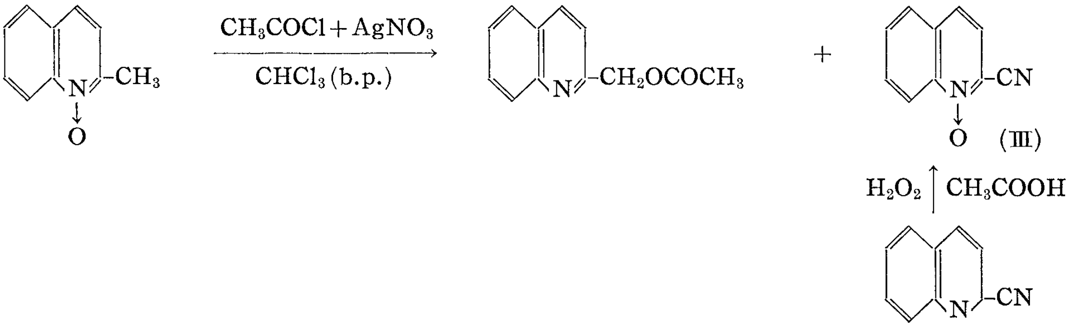
(I)

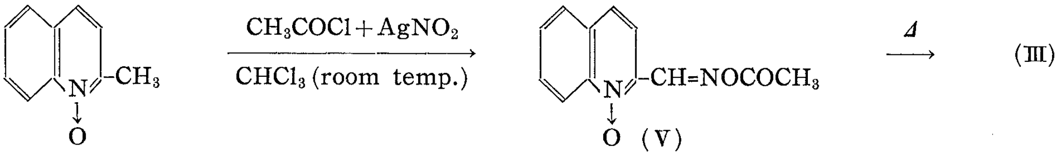


(II)



(IV)





(I) must be 2-cyano-3-nitroquinoline 1-oxide in view of the fact that (i) its molecular weight by the Rast method gave the monomolecular composition formula, (ii) infrared spectral curve showed a peak assigned to cyano group, and (iii) the product of catalytic

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[1] E. Ochiai, H. Tanida : This Bulletin, **4**, 313(1957).

[2] H. Tanida : Yakugaku Zasshi, **78**, 1079(1958).

[3] T. Kubota : *Ibid.*, **74**, 831(1954); Ann. Rept. Shionogi Research Lab., **6**, 31(1956).

[4] H. U. Daeniker, J. Druey : Helv. Chim. Acta, **41**, 2148(1958).

reduction has the same composition and molecular weight as 2-aminomethyl-3-aminoquinoline.

The above fact has shown that the active methyl was converted into a cyano group. The possible mechanism of this reaction may be proposed as follows: The first step should be the action of nitrous acid at the active methyl group of quinoline; in the second step, this nitroso derivative would change into oxime acylate, and the final step is the elimination of acetic acid from aldoxime acylate. The experiments described below were carried out in order to prove this mechanism.

When the chloroform solution of quinaldine 1-oxide with suspended silver nitrite was treated with acetyl chloride under cooling, slightly yellow needles (V), $C_{12}H_{10}O_3N_2$, m.p. 135.5°, were obtained. Its ultraviolet absorption spectrum was like that of 2-cyanoquinoline 1-oxide and showed the solvent effect, and its infrared spectrum exhibited characteristic peaks at 1771 and 1196 cm^{-1} which were respectively assigned to C=O(R-CO-O-C=C type) and C-O-N=. In addition to these spectral data, the crystals were quantitatively converted into (III) under heating in polar solvents. From a consideration of these data, (V) was concluded to be quinoline 1-oxide 2-aldoxime acetate.

The presence of an intermediate product proved the reliability of the above reaction mechanism. The improvement and application of this reaction is being studied at present.

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Microdetection of Reducing Sugars with 3,6-Dinitrophthalic Acid*

Several nitro compounds are widely used in the detection and estimation of reducing sugars, giving a specific coloration when heated with the sugar in alkaline medium. These involve picric acid,¹⁾ 3,5-dinitrosalicylic acid,²⁾ and 3,4-dinitrobenzoic acid.³⁾

In the writers' laboratory, 3,6-dinitrophthalic acid proved to give a more sensitive color reaction with reducing sugars than the reagents mentioned above. When the new reagent dissolved in aqueous sodium carbonate solution is heated with a small amount of a reducing sugar, an orange-red color appears in several minutes. This color changes rapidly to yellow, but if sodium thiosulfate is added to the reaction mixture, the color is stable for several days, and is easily distinguished from a blank test color which is only a faint yellow. In sodium hydroxide solution of the reagent, the color develops more rapidly but it is less stable, and the blank test gives a deeper color. Therefore, it is preferable to carry out this reaction in sodium carbonate solution.

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* cf. Part XVII on Organic Analysis, This Bulletin, in press (1959).
1) C.D. Braun : J. prakt. Chem., **96**, 411(1865).
2) J.B. Sumner, V.A. Graham : J. Biol. Chem., **47**, 5(1921).
3) E. Borel, H. Deuel : Helv. Chim. Acta, **36**, 801(1953).