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Oxidative Cyanation of Aromatic Amine Oxides

In the investigation of 1,6-naphthyridine 1,6-dioxide,[1] we found a reaction which was assumed to proceed through the intermediates shown in Chart 1.

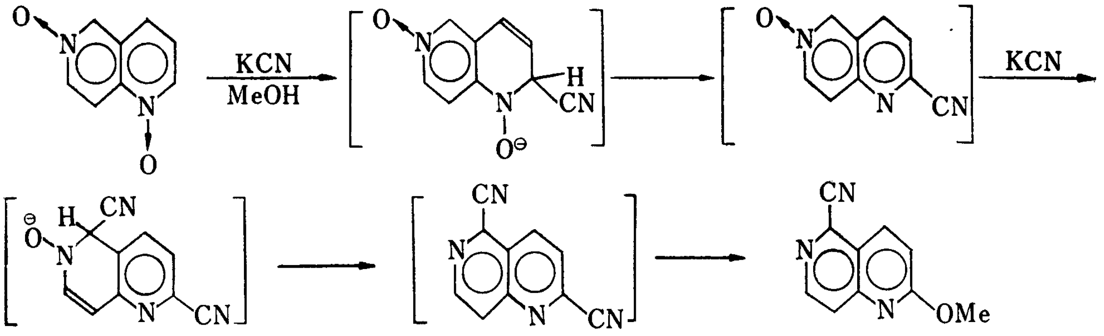

Chart 1

As 1,6-naphthyridine 1,6-dioxide was found to be very reactive to a nucleophile, it was thought that 2,5-dicyano-1,6-naphthyridine 1,6-dioxide should be obtained if the intermediates were oxidized with an appropriate oxidizing agent. Therefore, we tried this reaction in the presence of potassium ferricyanide. The result was as shown in Chart 2.

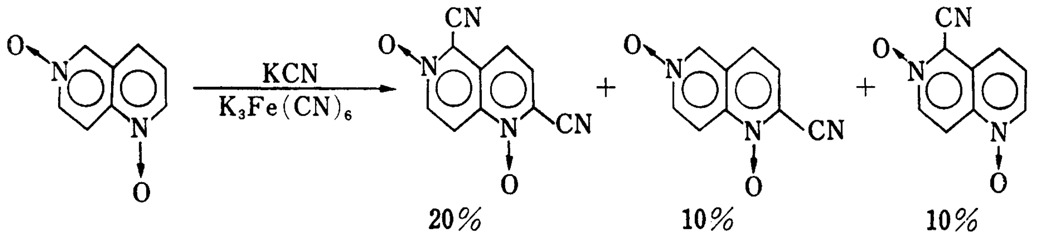

Chart 2

These products were very difficult to be obtained by the known two-step method, namely, the combination of the Reissert reaction and N-oxidation.

Then, the applicability of this reaction to other aromatic amine oxides was investigated and this reaction was found to be quite a general and excellent method to obtain α-cyano aromatic amine N-oxides from the corresponding N-oxides in one step.

The general procedure was as follows: to a saturated solution of potassium ferricyanide (1.5 mole eq.) and potassium cyanide (3—5 mole eq.) in water or dilute alcohol, N-oxides (1 mole eq.) were added and the reaction mixtures were stirred for 3 hours at designated temperatures. After cooling, the precipitated product was collected and recrystallized from an appropriate solvent.

The reaction conditions and results are summarized in Table I. It is obvious from Table I that the less the electron density of α-position is, the more reactive it is; namely, quinoline 1-oxide did not react at 25°, while 1,6-naphthyridine 1-oxide gave 2-cyano-compound at the same temperature.

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1) Y. Kobayashi, I. Kumadaki, and H. Sato, *Chem. Pharm. Bull.* (Tokyo), **17**, **2614** (**1969**).
2) Y. Kobayashi, I. Kumadaki, and H. Sato, *Chem. Pharm. Bull.* (Tokyo), **17**, **1045** (**1969**).
3) Y. Kobayashi, I. Kumadaki, and K. Morinaga, *Chem. Pharm. Bull.* (Tokyo), **17**, **1511** (**1969**).

Table I.

Reactant	Temp. (°C)	Position of introduced CN	mp (°C)	Yield (%)
Quinoline 1-oxide	75	2[a]	171	85
Isoquinoline 2-oxide	75	1[a]	207	85
1,6-Naphthyridine 1,6-dioxide[2]	25	2,5 (dicyano)[b]	248 (decomp.)	20
		2[b]	260 (decomp.)	10
		5[b]	257 (decomp.)	10
1,6-Naphthyridine 1-oxide[2]	25	2[b]	236 (decomp.)	80
1,6-Phenanthroline 6-oxide[3]	25	5[b]	220	82
Phenanthridine 5-oxide	50	6[a]	217	58

a) The structures were determined by admixture with authentic samples.
b) The structures were determined by elemental analyses and IR and NMR spectra.

A more quantitative consideration will be made using molecular orbital theory in a full paper.

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The Isolation of Neojusticin from *Justicia procumbens* Linn.

Justicidin A (I) and B (II), fish-killing components have been reported from *Justicia Hayatai* var. *decumbens*.[1] We now report the isolation of a new lignan named neojusticin from *J. procumbens* Linn. var. *leucantha* Honda (Japanese name, Kitsunenomago).

The ether extract of dried plant on chromatography afforded justicidin A and B as major components. Two of minor components were diphyllin (III)[2] and a new compound, neojusticin. Neojusticin, mp 273—275°, $C_{21}H_{14}O_7$ (M^+ calcd. 378.074, found 378.074) possesses one methoxy group (δ in $CDCl_3$ 4.31 (3H, s)), two methylenedioxy groups (6.06 (4H, s)), a γ-lactone methylene (5.10 (2H, s)), and five aromatic hydrogen atoms (7.70 (1H, s), 6.99 (1H, s), 6.95 (1H, d, $J=7$ cps), 6.78 (1H, s), and 6.72 (1H, d, $J=7$ cps)). UV $\lambda_{\max}^{CHCl_3}$ mμ (log ε): 263.5 (4.69), 298 (4.01), 319 (4.03), and 355 (3.47). IR $\nu_{\max}^{KBr}$ cm^{-1}: 1760 (γ-lactone carbonyl), 1605 (aromatic), 933 (methylenedioxy group).

The nuclear magnetic resonance (NMR) signals of aromatic hydrogens and ultraviolet (UV) spectrum of neojusticin resemble those of justicidin A (I), which means the both compounds should have the same substitution pattern. However, the NMR signal of γ-lactone methylene group (5.10) suggested system A rather than system B for neojusticin because Horii and his co-workers[3] pointed out that the methylene group in system A appears between 5.08

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1) K. Munakata, S. Marumo, K. Ohta and Y.-L. Chen, *Tetrahedron Letters*, **1965**, 4167; **1967**, 3821; *idem*, *Agr. Biol. Chem.*, 33, 610 (1969).
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3) Z. Horii, M. Tsujiuchi and T. Momose, *Tetrahedron Letters*, **1969**, 1079.