UDC 547.852.7.07:542.958.1

On Nitration of Cinnoline 1-Oxide

M. Ogata and *et al.*1) obtained two kinds of mono-N-oxide by N-oxidation of cinnoline using hydrogen peroxide in acetic acid and they have established the position of the N-oxides. The authors had also obtained two kinds of mono-N-oxide, which were coincident with Ogata's samples in melting point.

This paper deals with rearrangement reaction of cinnoline 1-oxide (I) with phosphoryl chloride and nitration of I with mixed acid and with benzoyl nitrate respectively.

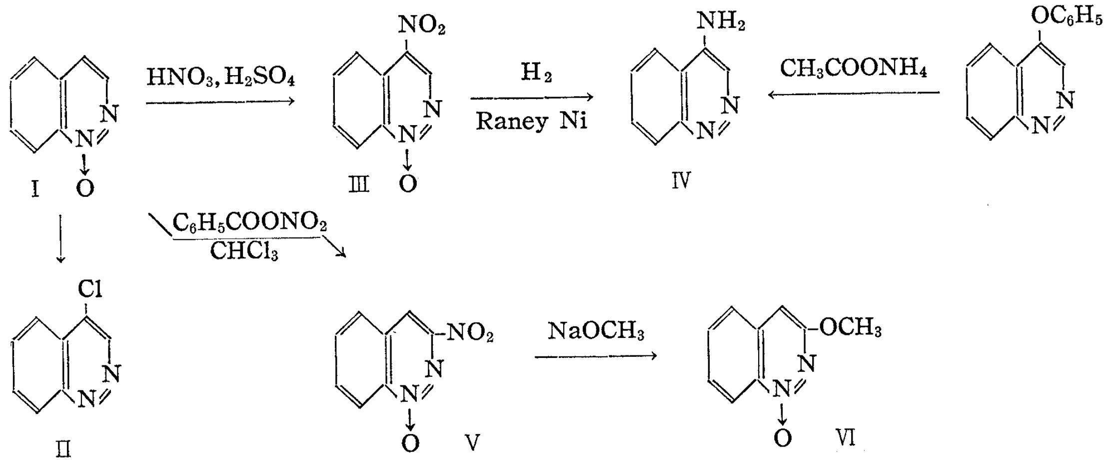

Chart 1.

On the treatment with phosphoryl chloride in chloroform at room temperature for 1 hour, cinnoline 1-oxide was converted into 4-chlorocinnoline (II), m.p. 76~77°, in 50% yield, as reported in pyridine and quinoline 1-oxides.2) This compound is also obtained by reaction of 4-cinnolinol with phosphoryl chloride and it was identified by infrared spectra and mixed melting point.

E. Ochiai and T. Okamoto3) reported that quinoline 1-oxide gave on warming with mixture of nitric and sulfuric acids at 65~75° the 4-nitro derivative, and at 0~10° 5- and 8-nitro derivatives were formed. Similarly cinnoline 1-oxide gave a mononitro compound (pale yellow needles, m.p. 161~162°. *Anal.* Calcd. for $C_8H_5O_3N_3$: C, 50.26; H, 2.64; N, 21.99. Found : C, 50.36; H, 2.86; N, 22.45.) by treatment with mixed acid at 70° for 3 hours in 35% yield with 24% recovery of the starting material. At 10~15° for 5 hours, a mononitro cinnoline 1-oxide was obtained in 6% yield with 67% recovery of I. Catalytic hydrogenation of this mononitro derivative over Raney's nickel gave monoamino cinnoline, m.p. 208~209°, in 75% yield, which was found to be identical with 4-aminocinnoline4) (IV) derived from 4-phenoxycinnoline and ammonium acetate by infrared spectra and mixed melting point, hence the structure of the mononitro derivative was confirmed to be 4-nitrocinnoline 1-oxide (III).

E. Ochiai and T. Kaneko5) found that quinoline N-oxide was nitrated with benzoyl nitrate to β-positions. When I was treated with freshly prepared benzoyl nitrate in chloroform solution, a mononitro derivative was obtained as yellow needles, m.p. 214~215° in 71% yield. (*Anal.* Calcd. for $C_8H_5O_3N_3$: C, 50.26; H, 2.64; N, 21.99. Found : C,

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1) M. Ogata, H. Kano, K. Tori : This Bulletim **10**, 1123 (1962).
2) B. Borbanski : Ber., **69**, 1113 (1936); *ibid.*, **71**, 578 (1938); T. Kato : Yakugaku Zasshi, **75**, 1236 (1955).
3) E. Ochiai, T. Okamoto : Yakugaku Zasshi, **70**, 384 (1950).
4) J. Keneford, K. Schofield, J. Simpson : J. Chem. Soc., **1948**, 358.
5) E. Ochiai, T. Kaneko : This Bulletin, **5**, 56 (1957); *ibid.*, **7**, 191, 195 (1959).

50.09; H, 2.79; N, 21.60.). For proof of its structure, it was converted into monomethoxycinnoline 1-oxide of m.p. 92.5~93.5° by treatment with sodium methoxide in 95% yield.

M. Ogata and *et al.*[1] reported that 3-chloro-5,6,7,8-tetrahydrocinnoline 1-oxide gave 3-methoxycinnoline 1-oxide (VI), m.p. 94~95°, by treatment with sodium methoxide and oxidation. VI was proved to be identical with the above mentioned monomethoxycinnoline 1-oxide by comparing the infrared spectra of monomethoxy compound with the authentic one which Dr. Ogata sent to us. This fact has shown that cinnoline 1-oxide was nitrated with benzoyl nitrate to 3-position. 3-Nitrocinnoline 1-oxide (V) gave an orange color in methanolic potassium hydroxide solution.

The authors are now studying on by-products in nitration with benzoylnitrate and further details will be reported later.

The authors express their gratitude to Prof. Emeritus E. Ochiai of the University of Tokyo for his helpful advices and to Drs. H. Kano and M. Ogata of Shionogi Research Laboratory, who kindly sent the infrared spectra of VI to us.

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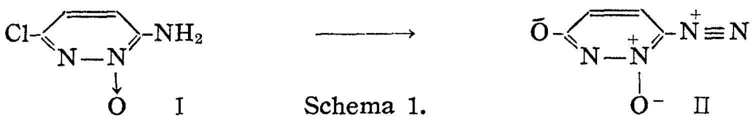
Einwirkungen von Essigsäureanhydrid auf Pyridazin-N-oxyden

Neuestens berichteten Itai und Nakajima,[1] da β man bei einer Diazotierung des 3-Amino-6-chlorpyridazin-2-oxydes (I) mit Natriumnitrit in Mineralsäure 3-Diazo-6-oxopyridazin-2-oxyd (II) erhält.



I Schema 1. II

Während wir bei dieser Nachprüfung kein identisches Resultat erhalten hatten, glückte es uns, durch die Diazotierung des I——durch langsam Hinzufügen des Natriumnitrites zur Lösung vom I in konz. Salzsäure unter Eiskühlung und Umrührung——3,6-Dichlorpyridazin-1-oxyd (III) in ziemlich guter Ausbeute zu erhalten. Diese Substanz wurde durch Mischprobe mit dem durch Oxydierung vom 3,6-Dichlorpyridazin mit Perbenzoesäure hergestellten III[2] als identisch erwiesen. Während wir Eisessig und Wasserstoff-hyperoxyd auf 3,6-Dichlorpyridazin einwirken liessen, um III nach dem anderen Verfahren zu erhalten, konnten wir kein Bezwecktes sondern nur ein Hydrolysierungsprodukt 6-Chlor-3(2*H*)-pyridazinon gewinnen. Beim Oxydieren vom 3,6-Dichlorpyridazin mit Perameisensäure, die durch Hinzufügen von etwas Schwefelsäure zur Mischung von Ameisensäure und Wasserstoff-hyperoxyd hergestellt wurde, ergaben III teilweise und 6-Chlor-3(2*H*)-pyridazinon als Hauptprodukt.

Nächst liessen sich 2-Acetoxy-6-chlor-3(2*H*)-pyridazinon (V) (Schmp. 126°. $C_6H_5O_3$-

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[1] T. Itai, T. Nakajima: Dieses Bulltin, **10**, 348 (1962).
[2] T. Nakagome: Yakugaku Zasshi, **82**, 246 (1962).