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134. Ikuo Suzuki, Masahiro Nakadate, Toshiaki Nakashima, and Natsuko Nagasawa: Studies on Cinnolines. V.*1 Cinnoline Dioxide.*2

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Cinnoline dioxide (Ⅳ) and indazole (Ⅴ) were obtained in addition to the monoxides on oxidation of cinnoline (Ⅰ) with hydrogen peroxide in acetic acid.

The structure of Ⅳ was confirmed by chemical and physico-chemical methods of UV, IR and NMR spectrometry and by polarographic reduction.

(Received February 21, 1966)

Ogata and his co-workers[1] obtained cinnoline 1- and 2-oxides by treatment of cinnoline with hydrogen peroxide in acetic acid, and investigated the nuclear magnetic resonance spectra of these cinnoline N-oxides.

The present report shows that oxidation of cinnoline with hydrogen peroxide in acetic acid gave cinnoline dioxide and indazole in addition to the monoxides.

When cinnoline (Ⅰ) was heated with hydrogen peroxide in acetic acid at 65~70° for 8 hours and the products were chromatographed over alumina,*4 cinnoline 1-oxide (Ⅱ), cinnoline 2-oxide (Ⅲ), and two other compounds, colorless needles, (Ⅳ) m.p. 235°, and colorless needles, (Ⅴ) m.p. 144~5° were isolated in 25.9, 49.4, 0.3, and 3.0% yields, respectively. Ⅴ was proved to be identical with an authentic sample of indazole synthesized by a known method.[2] Indazole was apparently formed by the ring contraction of cinnoline during oxidation, although the reaction mechanism is not clear as yet.[3] Ⅳ gave correct analytical data for cinnoline dioxide, $C_8H_6N_2O_2$.

Dioxide of diazines having adjacent nitrogens, such as pyridazine and phthalazine, is unknown, except for 4-methylcinnoline 1,2-dioxide[4] and benzo[*c*]cinnoline 5,6-dioxide.[5]

Ross and his collaborators[5a] reported that the sodium sulfide reduction of 2,2′-dinitrobiphenyl gave either benzo[*c*]cinnoline 5,6-dioxide or benzo[*c*]cinnoline 5-oxide, and that the treatment of 3,8-bis(trifluoromethyl)benzo[*c*]cinnoline with peracetic acid in chloroform gave 3,8-bis(trifluoromethyl)benzo[*c*]cinnoline 5-oxide.[5b] On the oxidation of benzo[*c*]cinnoline 5-oxide using hydrogen peroxide in acetic acid at 110~120° for 3 hours, we obtained benzo[*c*]cinnoline 5,6-dioxide in 7.2% yield. A similar oxidation of Ⅱ and Ⅲ gave the same compound, m.p. 235°, in 25.0 and 3.6% yields, which was proved to be identical with Ⅳ by mixed melting point determination and by comparison of their infrared spectra. Catalytic hydrogenation of Ⅳ over palladium charcoal afforded the known dihydrocinnoline[6] (Ⅵ), m.p. 83°, after absorption of 3 moles of hydrogen.

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*1 Part Ⅳ: This Bulletin, **14**, 816 (1966).

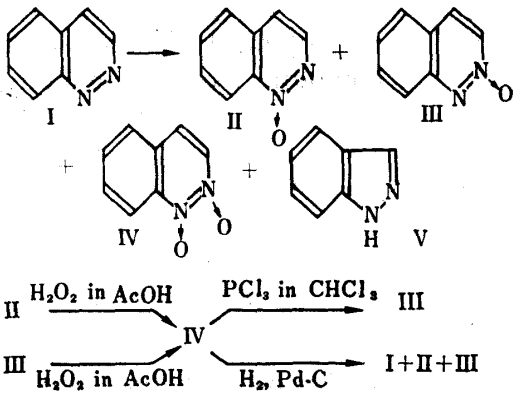
*2 Preliminary report of this work was published in Tetrahedron Letters, **1966**, 2899.

*3 Tamagawa-Yoga, Setagaya, Tokyo (鈴木郁生, 中館正弘, 中島利章, 長沢奈都子).

*4 An attempt to separate the products by the application of gas-chromatography using 5% SE-30 phase was unsuccessful and further examinations are now being made.

1) M. Ogata, H. Kano, K. Tori: This Bulletin, **11**, 1527 (1963).
2) Org. Syntheses, Coll. Vol. 3, 475 (1955).
3) I. Suzuki, *et al.*: This Bulletin, **13**, 713 (1965).
4) M. H. Palmer, E. R. R. Russell: Chem. & Ind., **1966**, 157.
5) *a*) S. D. Ross, G. J. Kahan, W. A. Leach: J. Am. Chem. Soc., **74**, 4122 (1965). *b*) S. D. Ross, I. Kunts: *Ibid.*, **74**, 1297 (1952).
6) M. Busch, A. Rast: Ber., **30**, 521 (1897).

From these results, IV seemed to be cinnoline dioxide and, in order to confirm its structure, following experiments were carried out.



According to Emerson and Rees,[7] benzo[*c*]cinnoline 5,6-dioxide hardly reacts with phosphorus trichloride and 82% of the dioxide is recovered unchanged.

When II and III were refluxed with a large amount of phosphorus trichloride in chloroform for 2 hours, cinnoline was obtained in 27.4 and 12.6% yields accompanied by recovery of the starting materials in 58 and 40% yields, respectively. On the other hand, treatment of IV with 1.7 moles of phosphorus trichloride in chloroform for 40 hours resulted in the formation of III in 10.1% yield, with recovery of the starting material in 72.7% yield. In addition, when the catalytic hydrogenation of IV over palladium charcoal in neutral solution was stopped after uptake of about one mole of hydrogen, I, II, III, and VI were formed in 3.9, 17.5, 64.6, and 3.4% yields, respectively. These results proved that IV is cinnoline dioxide. It is interesting that a large amount of III is formed and the end product is VI in the reduction of IV, in connection with the polarographic reduction to be described below.

Polarographic Reduction of Cinnoline Dioxide

The polarographic reduction of I, II, III, and IV was examined in aqueous solution at pH 2.0, 7.0, and 11.0, using saturated calomel electrode. The values of the half-wave potential, $-E_{1/2}$, are summarized in Table I.

Table I. Half-wave Reduction Potentials, $-E_{1/2}$ (V), measured against Saturated Calomel Electrode at 25°

pH	2.0	7.0	11.0		7.0		7.0
I	0.44	0.78	0.95	Benzo[*c*]cinnoline[a]	0.58	Phenazine[a]	0.36
II	0.48	0.83	1.01	Benzo[*c*]cinnoline monoxide[a]	0.69	Phenazine monoxide[a]	0.19
							0.36
III	0.50	0.86	1.06	Benzo[*c*]cinnoline dioxide[a]	0.60	Phenazine dioxide[a]	0.23
							0.36
IV	0.28	0.63	0.79				
	0.50	0.85	1.07				

a) Data by Ross and his collaborators,[5] at 20°

Previous workers[5] who investigated the polarography of N-oxides and N-dioxides of quinoxaline, phenazine, and benzo[*c*]cinnoline found that quinoxaline and phenazine were less readily reduced than their mono- and dioxides, whereas benzo[*c*]cinnoline was more easily reduced than either of the N-oxides. Benzo[*c*]cinnoline, its monoxides and dioxide show only one reduction wave, which fact probably indicates that these compounds are reduced to dihydrobenzo[*c*]cinnoline in one step.

As shown in Table I, cinnoline was more easily reduced than its monoxides in similar way as benzo[*c*]cinnoline series, and the wave obtained with cinnoline monoxides may correspond to the reduction of cinnoline monoxide to dihydrocinnoline. Further, IV was reduced more easily than the base itself, and the first half-wave potential for

7) T.R. Emerson, C.W. Rees: J. Chem. Soc., **1964**, 2319.

Ⅳ may correspond to the reduction of the dioxide to monoxide (probably 2-N-oxide). The half-wave potential of the second wave nearly coincides with the half-wave potential of cinnoline 2-oxide, and the ratio of the wave heights observed was 1:2. In view of these results, Ⅳ was probably reduced first to 2-N-oxide (2-electron step) which was then reduced to dihydrocinnoline (4-electron step). Although better polarograms are often obtained with acidic condition, we obtained nearly the same results with acidic, neutral, and alkaline conditions. The interesting feature of the reduction of Ⅳ is that Ⅳ is first reduced to cinnoline monoxide and then rapidly to dihydrocinnoline in polarographic reduction, and the same result was also obtained in catalytic hydrogenation.

Ultraviolet Spectra of Cinnoline Dioxide

Ultraviolet absorption spectra of Ⅱ and Ⅲ, and 4-methylcinnoline N-oxides were investigated by Ogata, *et al.*[1] who has shown that the spectra of 1-oxides are different from those of 2-oxides, and that the spectra of these N-oxides show a characteristic blue shift on increasing polarity of solvents, as already known.[8] As illustrated in Fig. 1, the ultraviolet absorption spectrum of Ⅳ shows strictly different curve from the spectra of monoxides. Solvent effect on the ultraviolet spectra of Ⅳ was examined by using dioxane, 95% ethanol, and water as the solvent (Fig. 2). The blue shift for Ⅳ increases characteristically with increasing solvent polarity, and this shift is greater than that in monoxides.

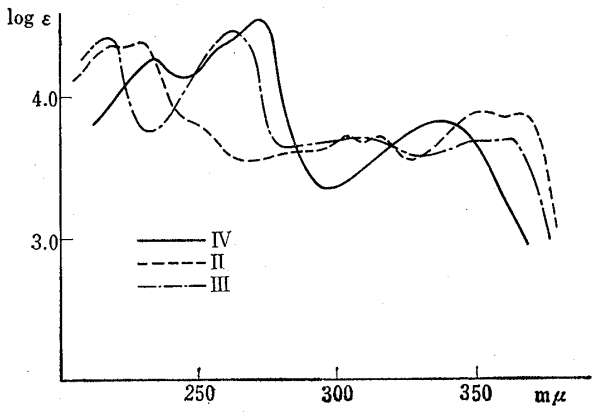


Fig. 1. Ultraviolet Absorption Spectra (in EtOH)

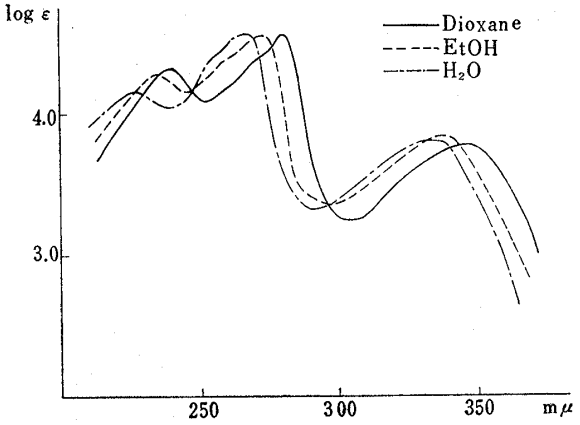


Fig. 2. Ultraviolet Absorption Spectra of Cinnoline Dioxide (Ⅳ)

Infrared Spectra of Cinnoline Dioxide

In general, it has been demonstrated that the band arising from N-O stretching vibration occurs in 1300 cm^{-1} region.[9] The bands at 1350 and 1348 cm^{-1} in the infrared spectra of Ⅱ and Ⅲ may be assigned to their N-O stretching vibrations, respectively. This assignment can be supported by the fact that these bands shift to lower frequency by addition of methanol to the chloroform solution.[9] In benzo[*c*]cinnoline 5,6-dioxide, the bands at 1399 and 1342 cm^{-1} were assigned by Lüttke[10] to the N-O stretching vibration. In addition, *cis*-1,4-dichloro-1,4-dinitrosocyclohexane (Ⅶ) exhibits two bands at 1399 and 1350 cm^{-1} which were attributed to the N-O stretching vibration from the number of *cis*- and *trans*-dinitroso dimers.[10] In connection with Ⅶ, it is

8) T. Kubota, H. Miyazaki: This Bulletin, **9**, 948 (1961).
9) H. Shindo: This Bulletin, **4**, 460 (1956).
10) W. Lüttke: Z. Electrochem., **61**, 976 (1957).

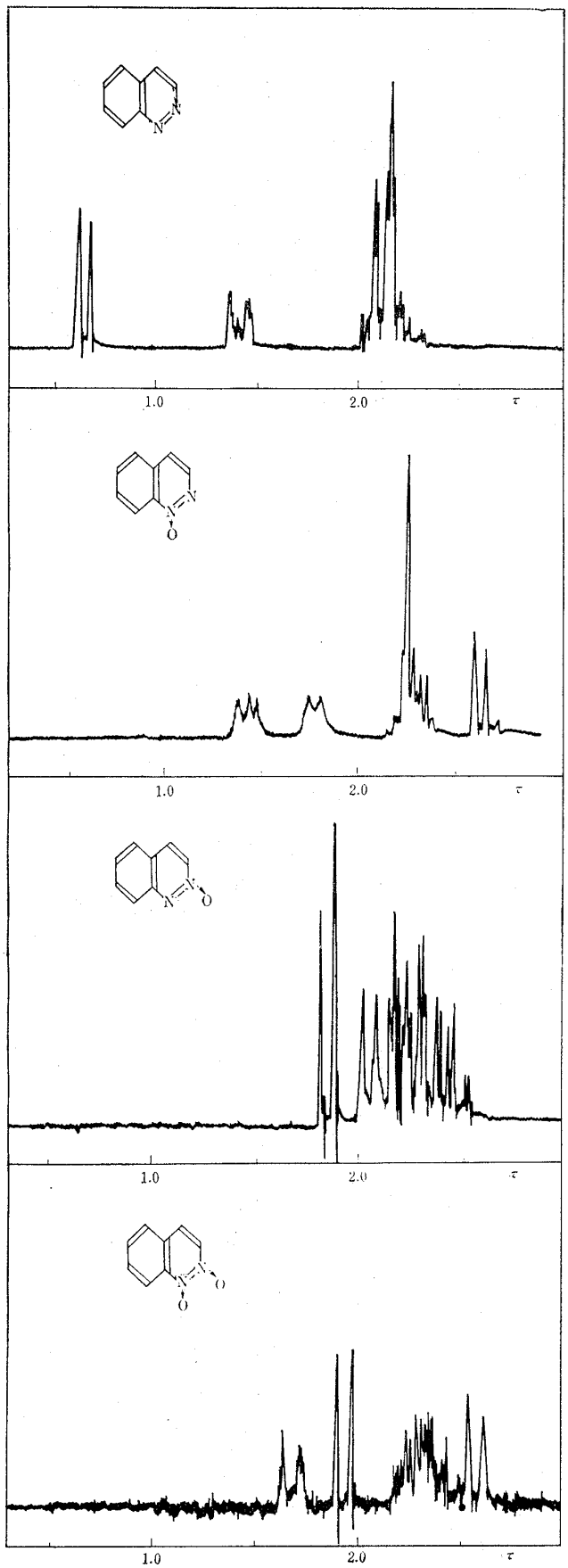


Fig. 3. Nuclear Magnetic Resonance Spectra of Cinnoline and its N-Oxides at 100 Mc. in $CDCl_3$.

considered that Ⅳ has an intramolecular nitroso dimer structure, that is, a structure having a *cis*-nitroso group within an aromatic ring. Consequently, two bands at 1403 and 1343 cm^{-1} in Ⅳ may be assigned to N-O stretching vibration, as expected. It has been reported[11] that cinnoline derivatives show a characteristic band near 1580 cm^{-1} and Ⅳ also shows a band at 1607 cm^{-1}.

Nuclear Magnetic Resonance Spectra of Cinnoline Dioxide

Ogata and his collaborators[1] reported the NMR spectra of cinnoline 1- and 2-oxides measured with 60 Mc. Our data at 100 Mc. are summarized in Table Ⅱ, and illustrated in Fig. 3.

Table Ⅱ. Nuclear Magnetic Resonance Spectral Parameters for Cinnoline Oxides

	τ_{H_3}	τ_{H_4}	τ_{H_8}	$J_{3,4}$	$J_{7,8}$	$J_{4,8}$
Cinnoline	0.72		1.47	5.5		1.0
Cinnoline 1-oxide	1.75	2.61	1.41	6.0	6.0	1.0
Cinnoline 2-oxide	1.85	2.05		7.0		1.0
Cinnoline dioxide	1.92	2.55	1.66	7.5	9.6	1.0

It has already been noted that N-oxidation of pyridine[12] and pyridazine[13] results in up-field shift of the signals of α- and γ-protons. As shown in Table Ⅱ, the NMR spectra of cinnoline mono-N-oxides appear at a higher field than that of cinnoline itself, and the spectrum of Ⅳ appears at a much higher field than that of cinnoline monoxides.

11) R. N. Castle, *et al.*: J. Am. Pharm. Assoc. Sci. Ed., **48**, 135 (1959).
12) A. R. Katritzky, J. M. Lagowsky: J. Chem. Soc., **1961**, 43.
13) Y. Kawazoe, S. Natsume: Yakugaku Zasshi, **83**, 523 (1963).

It can be considered that in cinnoline the signal of the proton H_3 attached to the carbon atom adjacent to nitrogen appears at the lowest field. Therefore, the signal at 0.72τ can be assigned to the proton H_3 in I. Since the electron charge density on the C_4 atom is higher than those on other carbons in cinnoline ring by π-electron density calculation,[14] the signal of the proton H_4 of I should appear at a higher field than the signals of other protons. Therefore, the signal at 1.47τ may be assigned to the proton H_8*[5] in I.

As shown in Fig 3, the spectrum of II exhibits three characteristic peaks at 1.41τ, 1.75τ and 2.61τ. As has already been reported,[1] the proton at a *peri*-position to the N-oxide group of II shows signal peak at a lower field than other signals, owing to the anisotropy of the N-oxide group, and accordingly, the signal at 1.41τ is due to the proton H_8.

It is expected that the signal of H_4 proton appears at the highest field (2.61τ), owing to the high electron density of 4-position in II by mesomeric effect of N-oxide group, and the peak at 1.75τ corresponds to the proton H_3 at a carbon atom adjacent to the nitrogen. The coupling constants $J_{3,4}$ and $J_{7,8}$ in II were found to have 6.0 c.p.s.

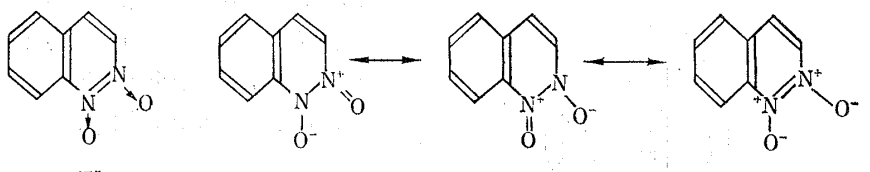
In III, the signal peak at 1.85τ may be assigned to the proton H_3, because the magnetic anisotropy of the N-O group gives a greater effect on 3-position than the mesomeric effect of N-O group. The signal of the proton H_4 in III appears at a lower field than that of II. This assignment to the chemical shifts of II and III is not inconsistent with Ogata's interpretation. All the values of spin-spin coupling constants, $J_{3,4}$ obtained as shown in Table II, are reasonable for ortho couplings of ring protons and are similar to those of Ogata's data.

Tori, *et al.*[15] have reported that in the NMR spectra of quinoline 1-oxide and its derivatives, the proton at a *peri*-position to the N-O group, like that at an *ortho*-position, appears at a lower field than those of other signals, owing to the anisotropic effect of the N-O group, and the chemical shifts assigned in the order 8< 2< 4< 3. Since the proton H_8 and H_3 in IV are affected by the anisotropic effect of the 1-oxide and 2-oxide, respectively, similar relation as in quinoline N-oxide may be found in cinnoline dioxide. Therefore, the peaks at 1.66τ and 1.92τ in the spectrum of IV can be assigned respectively to the proton H_8 and H_3 in IV.

On the other hand, the π-electron charge density on the C_4 atom in IV is increased by the mesomeric effect of the 1-oxide group and, accordingly, the signal peak of 2.55τ can be assigned to the proton H_4. The signal peak of the H_4 proton of IV appears at a lower field than that of II and a higher field than that of III. The values of the coupling constant $J_{3,4}$ are reasonable for ortho coupling of the ring proton, and support the above assignment.

From the evidence obtained by chemical and physicochemical data stated above, we concluded that IV was cinnoline 1,2-dioxide.

Structure of benzo[*c*]cinnoline 5,6-dioxide has been discussed by Ross,[5] and by Emerson and Rees.[6] Ross suggested that benzo[*c*]cinnoline 5,6-dioxide may exist in a



IV

*5 Recently, M. H. Palmer and B. Semple (Chem. & Ind., **1965**, 1766) reported that the chemical shifts for cinnoline (in τ-values) were in the order of 3<8<4<others.

14) H. C. Loguet-Higgins, C. A. Coulson : J. Chem. Soc., **1949**, 971.

15) K. Tori, M. Ogata, H. Kano : This Bulletin, **11**, 681 (1963).

dinitroso structure from the fact it is a colorless solid which dissolves to give a colored solution. However, the chemical and physical properties of IV, inertness towards phosphorus trichloride, and formation of dioxide from cinnoline and its monoxide by N-oxidation, and its high melting point, lack of color in the solid state and in solution, are incompatible with the presence of a free nitroso group. These results suggested that IV is stabilized by many resonance structures.

Experimental*6

Oxidation of Benzo[*c*]cinnoline 5-Oxide——A mixture of 500 mg. of benzo[*c*]cinnoline 5-oxide, 10 ml. of AcOH, and 2 ml. of 50% H_2O_2 was heated at 110~120° for 3 hr. on an oil bath. To the reaction mixture, 10 ml. of H_2O was added, AcOH was evaporated under reduced pressure, and this procedure was repeated twice. After basification with Na_2CO_3, the solution was extracted with $CHCl_3$. The $CHCl_3$ layer was dried over anhyd. Na_2SO_4 and evaporated. The residue was dissolved in benzene containing 10% $CHCl_3$ and chromatographed on alumina. From the first fraction eluted with the same solvent, yellow crystals were obtained. Recrystallization from EtOH gave benzo[*c*]cinnoline 5-oxide as pale yellow needles. m.p. 138~140°. Yield, 356 mg. (71.2%).

From the second fraction eluted with benzene containing 50% $CHCl_3$, yellow crystals were obtained. Recrystallization from EtOH gave benzo[*c*]cinnoline 5,6-dioxide as colorless needles, m.p. 231~232°(decomp.). Yield, 38.7 mg. (7.2%). On admixture of this compound with benzo[*c*]cinnoline 5,6-dioxide derived from the known method,[5] no depression of the melting point was observed and the IR spectra (in Nujol) of those two compounds were quite identical.

Oxidation of Cinnoline (I)——a) With 30% H_2O_2 at 65~70°: A mixture of 1.1 g. of I, 8 ml. of AcOH, and 4 ml. of 30% H_2O_2 was heated at 65~70° for 4 hr. on a water bath, further 4 ml. of 30% H_2O_2 was added, and the mixture again heated at the same temperature for 4 hr. To the reaction mixture, 20 ml. of H_2O was added, AcOH was evaporated under reduced pressure, and this procedure was repeated twice. The solution was basified with Na_2CO_3 and extracted with $CHCl_3$. The $CHCl_3$ layer was dried over anhyd. Na_2SO_4 and evaporated. The residue was dissolved in benzene-hexane and chromatographed on alumina. From the first fraction eluted with hexane containing 50% benzene, crystals were obtained. Recrystallization from benzene gave cinnoline 1-oxide (II) as pale yellow plates, m.p. 110~111°. Yield, 0.32 g. (25.9%). UV λ_{max}^{EtOH} mμ (log ε): 230 (3.70), 315 (4.03), 351 (3.89), 367 (3.87).

The second fraction eluted with benzene gave white crystals. Recrystallization from benzene gave cinnoline 2-oxide (III) as white needles, m.p. 122~123°. Yield, 0.61 g. (49.4%). UV λ_{max}^{EtOH} mμ (log ε): 262 (4.47), 267 (shoulder), 310 (3.68), 352 (3.69), 361 (3.69).

The third fraction eluted with benzene containing 50% $CHCl_3$ afforded 35 mg. of white crystals. This fraction showed two spots by thin-layer chromatography on silica-gel G. To this crystals, 50 ml. of ether was added and filtered. Recrystallization of ether-insoluble residue from EtOH gave cinnoline 1,2-dioxide (IV) as colorless needles, m.p. 235°(decomp.). Yield, 4 mg. (0.3%). *Anal.* Calcd. for $C_8H_6O_2N_2$: C, 59.26; H, 3.73; N, 17.28. Fonud: C, 59.49; H, 3.91; N, 17.12. UV λ_{max}^{EtOH} mμ (log ε): 234 (4.26), 258 (4.35), 273 (4.55), 340 (3.81).

Recrystallization of ether-soluble crystals from benzene-petroleum ether gave indazole (V) as colorless needles, m.p. 144~145°. Yield, 30 mg. (3.0%). UV λ_{max}^{EtOH} mμ (log ε): 251.5 (3.63), 258 (3.61), 280 (3.57), 285 (3.65), 290 (3.64), 295.5 (3.60). No depression of melting points occurred on admixture of this compound with indazole derived from the known method,[3] and the IR spectra (in KBr disk) of these two compounds were identical.

b) With 50% H_2O_2 at 110~120°: A mixture of 80 mg. of I, 10 ml. of AcOH, and 2 ml. of 50% H_2O_2 was heated at 110~120° for 5 hr., further 4 ml. of 50% H_2O_2 was added, and again heated at the same temperature for 7 hr. When the reaction mixture was treated as in (a), 240 mg. of III, 250 mg. of the mixture of II and III, and 114 mg. (12.8%) of IV was obtained.

Oxidation of Cinnoline 1-Oxide (II)——A mixture of 90 mg. of II, 2 ml. of AcOH, and 0.5 ml. of 50% H_2O_2 was heated at 110~120° for 3 hr., further 0.5 ml. of 50% H_2O_2 was added, and again heated at the same temperature for 3 hr. To the reaction mixture, 5 ml. of H_2O was added, AcOH was evaporated under reduced pressure, and this was repeated twice. The residue was crystallized from Me_2CO-benzene to give 20 mg. of gray needles, m.p. 227°. Recrystallization from the same solvent gave IV as colorless needles, m.p. 235°. The mother liquor was passed through a column of Al_2O_3 and eluted with benzene. The first eluted product was identified as II. Yield, 45 mg. (50%). The second eluted product, 5 mg., was identical with IV. Total yield 25 mg. (25.0%).

*6 Melting points are uncorrected.

Oxidation of Cinnoline 2-Oxide (III)——A mixture of 760 mg. of III, 10 ml. of AcOH, and 6 ml. of 50% H_2O_2 was heated at 110~120° for 8 hr. When the reaction mixture was treated as described in oxidation of II, 405 mg. of III (Yield, 53.3%) was recovered and 30 mg. of IV (Yield, 3.6%) was obtained.

Deoxygenation of Cinnoline 1-Oxide (II)——To a solution of 52 mg. of II in 2 ml. of $CHCl_3$, a mixture of 1 ml. of PCl_3 and 10 ml. of $CHCl_3$ was added at room temperature and the mixture was refluxed for 2 hr. When cooled, the mixture was poured on crushed ice, neutralized with 10% Na_2CO_3 solution, and extracted with $CHCl_3$. The solvent was distilled off from the extract, the residue was dissolved in benzene containing 50% hexane, and chromatographed on alumina. From the first fraction eluted with the same solvent, greenish oil (13 mg.) was obtained. EtOH solution of picric acid, was added to the oil dissolved in EtOH and the mixture refluxed for 1 min. The picrate, m.p. 194~195°, was obtained in 35 mg. Yield (27.4%, as cinnoline). On admixture of this picrate with an authentic cinnoline picrate, no depression of melting point was observed, and the IR spectra of the two samples were identical.

The second fraction eluted with benzene gave II which recrystallized from benzene to pale yellow prisms, m.p. 111~112°. Yield, 30 mg. (58%).

Deoxygenation of Cinnoline 2-Oxide (III)——To a solution 100 mg. of III in 2 ml. of $CHCl_3$, a mixture of 1 ml. of PCl_3 and 10 ml. of $CHCl_3$ was added at room temperature and the mixture was treated as described in deoxygenation of II. Greenish oil (11 mg.) and white crystals were obtained. The oil gave a picrate of m.p. 194~195°. Yield, 31 mg. (12.6%, as cinnoline). On admixture of this picrate with an authentic cinnoline picrate, no depression of the melting point was observed and IR spectra of the two samples were identical. White crystals were recrystallized from benzene to give colorless needles (III), m.p. 122~123°. Yield, 40 mg. (40%).

Deoxygenation of Cinnoline Dioxide (IV)——To a solution of 55 mg. of IV in 25 ml. of $CHCl_3$, a mixture of 80 mg. (1.7 mole) of PCl_3 and 25 ml. of $CHCl_3$ was added at room temperature. The mixture was treated as described in deoxygenation of II and chromatographed on alumina. The first eluate with benzene gave 5 mg. (10.1%) of III and the second eluate with $CHCl_3$ afforded 40 mg. (73%) of IV.

Catalytic Hydrogenation of Cinnoline Dioxide (IV)——a) A solution of 190 mg. of IV and 20% Pd-C in 8 ml. of MeOH was shaken in H_2 stream. After absorption of 3 moles of H_2, the catalyst was removed and the solvent was evaporated. Recrystallization of the residue from ether-hexane gave 130 mg. (84%) of pale yellow needles, m.p. 82~83°, undepressed on admixture with dihydrocinnoline (VI) derived from an authentic method, IR spectra of these two compounds were identical.

b) A solution of 0.5 g. of IV and Pd-C prepared from 7.6 ml. of 1% $PdCl_2$ solution and 0.4 g. of charcoal in 100 ml. of EtOH was shaken in H_2 stream. The reduction was stopped after absorption of 1 mole of H_2 (70 ml.) and the catalyst was filtered off. EtOH was evaporated, the residue was dissolved in hexane-benzene, and chromatographed on alumina. The crystals from the first fraction eluted with the same solvent, were recrystallized from EtOH to VI as pale yellow needles, m.p. 80~82°. Yield, 14 mg. (3.4%).

The second fraction eluted with the same solvent gave a yellow oil, to which, dissolved in EtOH, EtOH solution of picric acid was added dropwise. Picrate, m.p. 194~195°. Yield, 43 mg. (4%, as cinnoline). On admixture of this picrate with an authentic cinnoline picrate, no depression of melting point was observed.

The third eluate with the same solvent gave 79 mg. (17.5%) of II, m.p. 110~111°, and the fourth eluate with benzene afforded 291 mg. (64.6%) of III, m.p. 122~123°.

Catalytic Hydrogenation of II and III Mixture——A solution of 0.55 g. of a mixture of II and III and Pd-C, prepared from 9.5 ml. of 1% $PdCl_2$ solution and 0.5 g. of charcoal in 50 ml. of EtOH, was shaken in H_2 stream. After a complete absorption of H_2 (2 moles), the catalyst was removed, EtOH was evaporated, and the residue was recrystallized from EtOH to VI as pale yellow needles, m.p. 80~81°. Yield, 470 mg. (94.5%).

Polarography——A Yanagimoto polarograph PA-101 with Photographic recorder was used. Half-wave potentials were measured with respect to the saturated calomel electrode. The polarographic cell used was an H-type cell and general procedure was conventional. Reduction were measured at 25°±1° in nitrogen with *ca.* $10^{-4}M$ water-ethanol solutions in a buffer solution of pH 2.0 (Clark-Lubs buffer solution), 7.0 (McIlvaine buffer solution), and 11.0 (Sörensen buffer solution). The pH of these buffer solutions were checked with a glass electrode. Half-wave potentials, $-E_{1/2}$, were estimated graphically. The values recorded in Table I are the means of three to five determinations. Diffusion currents were not measured.

All the NMR spectra were taken with Varian HR-100 NMR spectrometer system on 1~4% (w/v) solution in $CDCl_3$ containing about 1% tetramethylsilane as an internal reference. The chemical shifts are expressed as τ-units and coupling constants in c.p.s.

The ultraviolet absorption spectra were taken with Hitachi recording spectrophotometer using 10 mm. cell at 25°.

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