$NaHCO_3$ solution and the insoluble portion was crystallized from EtOH with charcoal to dull pale yellow needles, m.p. 225~227°. Yield, 1.1 g. It is fairly soluble in hot EtOH and cold glacial AcOH. *Anal.* Calcd. for $C_{13}H_9O_3N$: C, 68.72; H, 3.99; N, 6.17. Found: C, 68.90; H, 4.13; N, 5.85.

3-Bromo-5,6-dihydro-6-methyl-2*H*-pyrano[3,2-*c*]quinoline-2,5-dione (IV)—A 10% bromine-glacial AcOH solution (6 cc.) was added to (III) (0.5 g.) dissolved in glacial AcOH (25 cc.), and this was sealed in a glass tube. After standing a week, the content was diluted with water and the crystals that separated out (0.5 g.) were collected, washed with water, and dried. It crystallized from glacial AcOH to pale yellow needles, melting clearly at 260° (fusing mostly into liquid at 248°). It is sparingly soluble in EtOH aad soluble in hot glacial AcOH. *Anal.* Calcd. for $C_{13}H_8O_3NBr$: C, 51.00; H, 2.63; N, 4.58. Found: C, 50.55; H, 2.59; N, 4.42.

4,5-Dihydro-5-methyl-4-oxofuro[3,2-*c*]quinoline-2-carboxylic Acid(V)—A mixture of (IV) (0.7 g.) and 10% KOH solution (60 cc.) was heated on a water bath during 1 hr. After cool, the content was diluted with water and filtered. The pale yellow crystals that separated out from the filtrate by acidification with dil. H_2SO_4 were treated immediately with $NaHCO_3$ solution. The $NaHCO_3$-soluble portion was acidified with dil. H_2SO_4 and the separated crystals were crystallized from dehyd. EtOH with charcoal to colorless needles (0.4 g.), mp. over 300°. *Anal.* Calcd. for $C_{13}H_9O_4N$: C, 64.20; H, 3.73; N' 5.76. Found: C, 63.70; H, 3.97; N, 5.81.

Methyl 4,5-Dihydro-5-methyl-4-oxofuro[3,2-*c*]quinoline-2-carboxylate (VI)—(V) (0.2 g.) was methylated with CH_2N_2 in MeOH by the usual procedure. Colorless needles, m.p. 207~208° (from EtOH). *Anal.* Calcd. for $C_{14}H_{11}O_4N \cdot H_2O$: C, 61.09; H, 4.76; N, 5.09. Found: C, 61.26; H, 4.12; N, 4.97.

5-Methylfuro[3,2-*c*]quinolin-4(5*H*)-one (I)—A mixture of (V) (0.2 g.), pure quinoline (3 cc.), and Cu powder (0.1 g.) was heated at 170~180° for 30 mins., further at 180~200° for 20 mins. After cool, the content was dissolved in 10% HCl and filtered. The filtrate was shaken with $CHCl_3$ and the solvent was removed by distillation. The $NaHCO_3$-insoluble matter of $CHCl_3$ residue was recrystallized from dil. EtOH to form colorless needles, m.p. 132~133°, which showed no depression on admixture with the specimen synthesized previously by another method.[2]

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Itiro Yosioka and Reiko Ashikawa: Studies on Phenazines. XIV[1]. Wohl-Aue Reaction of *m*-Anisidine and *m*-Nitroanisole.

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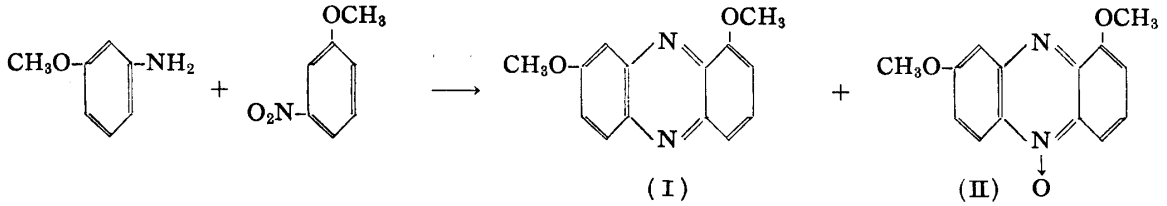
It was shown in the previous papers[2] of this series, that all the isomers of dimethoxyphenazine were synthesized by the improved Wohl-Aue method, but at that time condensation of *m*-anisidine and *m*-nitroanisole was not carried out.

This time *m*-anisidine was condensed with *m*-nitroanisole by the aid of potassium hydroxide in toluene solution and 1,8-dimethoxyphenazine (I) and its 5-N-oxide (II) were obtained. The latter was deoxygenated by heating with glacial acetic acid and zinc powder to form 1,8-dimethoxyphenazine.



(I) (II)

In this reaction the anticipated 1,6- and 2,7-dimethoxyphenazines were not produced.

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Experimental

Wohl-Aue Reaction of *m*-Anisidine and *m*-Nitroanisole—A mixture of *m*-anisidine (16.5 g.), *m*-nitroanisole (17 g.), and powdered KOH (40 g.) was boiled in toluene (150 cc.) under reflux in an oil bath for 3 hrs. After the reaction, toluene solution was removed by steam distillation. The crude crystalline substance deposited in the remaining aq. solution was filtered, dried, dissolved in benzene, and purified by chromatography on alumina. The first eluate contained no crystalline substance. From the next eluate yellow needles of m.p. 150~153° (from benzene) were obtained. Yield: 1.6 g. This was found to be identical with 1,8-dimethoxyphenazine (I) by mixed fusion. *Anal.* Calcd. for $C_{14}H_{12}O_2N_2$: C, 70.00; H, 5.00. Found: C, 69.81; H, 5.24.

From the last eluate 1,8-dimethoxyphenazine 5-N-oxide as yellow needles, m.p. 205~210° (from benzene), were obtained. Yield: 3.3 g. *Anal.* Calcd. for $C_{14}H_{12}O_3N_2$: C, 65.62; H, 4.68. Found: C, 65.24; H, 5.07.

Deoxygenation of 1,8-dimethoxyphenazine 5-N-oxide—A mixture of 1,8-dimethoxyphenazine 5-N-oxide (0.1 g.), zinc powder (0.1 g.), and glacial acetic acid (1 cc.) was warmed on a water bath for 15 mins. Water was added to this reaction mixture, the precipitate deposited was extracted with benzene, and purified on alumina. Yellow needles of m.p. 150~152° (from benzene) were obtained. Yield: 0.05 g. This was found to be identical with the authentic specimen of 1,8-dimethoxyphenazine by mixed melting point determination.

Summary

m-Anisidine and *m*-nitroanisole were condensed by Wohl-Aue method and 1,8-dimethoxyphenazine and its 5-N-oxide were obtained.

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Zen-ichi Horii, Teiji Tanaka, and Yuriko Murakami: Itaconic Acid in Organic Chemistry. I. Synthesis of 2-Methyl-1,4-naphthoquinone (Menadione).

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Until some years ago, itaconic acid was not easily obtainable but it is at the present time easily available because the economical preparation of this acid by fermentation of molasses has been found feasible. We noticed this acid useful as a starting material for synthetic organic chemistry, as its price was cheap and it had chemically interesting groups such as vinyl in its molecule. As an initial research of this series, we studied the preparation of menadione (2-methyl-1,4-naphthoquinone) from itaconic aicd. The reaction scheme adopted by us was as follows:

The hydrogenation of itaconic acid (I) to methylsuccinic aicd (II) was carried out according to the method of Dixon.[1] 2-Methyl-1-tetralone (VIII) was prepared by modification of the method of Alexander.[2] (V) was obtained by the Clemmensen reduction of 3-benzoyl-2-methylacrylic acid (VII), which was prepared by the reaction of itaconic anhydride and benzene in the presence of aluminum chloride.[1] The catalytic reduction of itaconic acid to methylsuccinic acid could be avoided by this method but the over-all yields (based on itaconic acid) of these methods were nearly the same.

Formerly, Sah[3] synthesized menadione (IX) by the chromium trioxide oxidation of 2-methylnaphthalene, which was prepared by the Clemmensen reduction of (VIII), followed

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