[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF KITASATO INSTITUTE]

REDUCTION OF NITROSOPHENOL BY IRON AND HYDROCHLORIC ACID

BY KONOMU MATSUMURA AND CHUSABURO SONE

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In a study of quinoline syntheses, 7-amino-5-acetyl-8-hydroxyquinoline was desired. On treating the corresponding nitroso compound either with stannous chloride and hydrochloric acid or with iron powder and dilute alcohol in the presence of a trace of hydrochloric acid, owing to side reactions, presumably, the anticipated amino compound was formed only in a poor yield, whereas the nitroso compound, on reduction by iron powder and dilute hydrochloric acid, gave the dihydroxyl compound in a satisfactory yield.

The diazo reaction which is not shown by the nitroso compound may serve as evidence that the nitroso radical, now introduced, occupies the position adjacent to the hydroxyl radical.

From 5-nitroso-8-hydroxyquinoline or *p*-nitrosophenol, by analogy, we could isolate the corresponding dihydroxyl compounds in satisfactory yields, while from *p*-nitrophenol, the corresponding aminophenol, and hydroquinone and from *o*-nitrophenol, *o*-aminophenol only could be isolated.

Experimental

7-Nitroso-5-acetyl-8-hydroxyquinoline.—On the gradual addition of a solution of sodium nitrite (3.2 g.) in water (30 cc.) to a solution of 5-acetyl-8-hydroxyquinoline (8 g.)[1] in a mixture of glacial acetic acid (25 g.) and water (35 cc.) at 0° with stirring, yellow crystals separated. They were filtered after being allowed to stand for several hours at the room temperature (yield, 7.8 g.) and carefully recrystallized from glacial acetic acid into yellowish-brown prisms which begin to decompose at 180° and decompose thoroughly at 190–195°. It is soluble in the usual organic solvents, water or dilute mineral acids. It gives a light brown color reaction with ferric chloride, but no color reaction with diazotized sulfanilic acid.

Anal. Calcd. for $C_{11}H_8O_3N_2$: N, 12.96. Found: N, 12.60.

7-Amino-5-acetyl-8-hydroxyquinoline.—7-Nitroso-5-acetyl-8-hydroxy-quinoline (2.5 g.) was reduced with stannous chloride (5.4 g.) and concd. hydrochloric acid (13.5 g.) in the presence of glacial acetic acid (30 g.), and the reduction product isolated in the usual way; yield, 0.7 g. It forms light yellow needles from ether, melting at 148–149° (dec.). It is soluble in the usual organic solvents.

Anal. Calcd. for $C_{11}H_{10}O_2N_2$: C, 65.35; H, 4.95; N, 13.86. Found: C, 65.56; H, 5.34; N, 13.59.

The picrate gives orange needles from alcohol, decomposing at 201–222°.

Anal. Calcd. for $C_{11}H_{10}O_2N_2 \cdot C_6H_3O_7N_3$: N, 16.21. Found: N, 16.27.

The hydrochloride gives orange needles, sintering at 145°. It is easily soluble in water.

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[1] Matsumura, THIS JOURNAL, **52**, 4433 (1930).

5-Acetyl-7,8-dihydroxyquinoline.—3.75 g. of 7-nitroso-5-acetyl-8-hydroxyquinoline was dissolved in a hot solution (95°) of 27 g. of concd. hydrochloric acid in 900 cc. of water, 5 g. of iron powder was then gradually added during one hour with constant agitation, and the agitation continued for one hour more at the same temperature. On concentrating the reaction fluid, after filtration, under diminished pressure, 3.25 g. of yellow needles of the hydrochloride separated out. This was dissolved in water and on neutralization with sodium carbonate, the deep red free base separated. On drying in a desiccator, it lost its red color and became colorless. It crystallizes as colorless prisms from alcohol, m. p. 235–236°. On dissolving in dilute hydrochloric acid and alkalifying, the initial red-colored substance can be regenerated. The red substance, on recrystallization from hot water, gives scarlet red needles.

Anal. Water of crystallization. Calcd. for $C_{11}H_9O_3N \cdot 1.5\ H_2O$: H_2O, 11.74. Found: H_2O, 11.07.

The red substance, on recrystallization from dilute alcohol which contains some acetic acid, gives deep red prisms or columns; m. p. 241–242° (dec.). It contains no water of crystallization and does not decolorize on drying at 100° but gradually decolorizes near its melting point. Its mixed melting point with the colorless form is at 236–240°. On working up its alcoholic solution, after treatment with sulfur dioxide or sodium hydrosulfite, the initial substance can be recovered. It is moderately soluble in the usual organic solvents, dilute mineral acid or alkali. The solution in concd. sulfuric acid is light yellow. It gives a deep green color reaction with ferric chloride and a red color reaction with diazotized sulfanilic acid, only in highly concentrated solution.

Anal. Calcd. for $C_{11}H_9O_3N$: C, 65.02; H, 4.43; N, 6.89. Found: C, 65.40; H, 4.89; N, 7.00, 6.85.

The hydrochloride gives lemon-yellow needles from hydrochloric acid (10%), m. p. 280–305° (decomp.). It is difficultly soluble in alcohol but easily soluble in water.

Anal. Calcd. for $C_{11}H_9O_3N \cdot HCl$: C, 55.12; H, 4.18; N, 5.85. Found: C, 55.41; H, 4.51; N, 5.83.

The oxime gives red needles from dilute alcohol which contains some acetic acid; these decompose at 215–220° without melting.

Anal. Calcd. for $C_{11}H_{10}O_3N_2$: N, 12.84. Found: N, 12.55.

5-Acetyl-7,8-diacetoxyquinoline.—A mixture of 0.2 g. of 5-acetyl-7,8-dihydroxyquinoline (red form), 0.5 g. of sodium acetate and 2 g. of acetate anhydride was heated on a water-bath for one hour. On pouring the cooled reaction fluid on crushed ice, colorless crystals separated. These were recrystallized from ether into colorless columns, m. p. 121–122°, yield, 0.2 g. It is easily soluble in alcohol, benzene, ether or dilute hydrochloric acid.

Anal. Calcd. for $C_{15}H_{13}O_5N$: C, 62.72; H, 4.57; N, 4.88. Found: C, 62.59; H, 5.00; N, 4.97.

5,8-Dihydroxyquinoline.—2.85 grams of 5-nitroso-8-hydroxyquinoline was reduced in exactly the same manner that was described for 5-acetyl-7,8-dihydroxyquinoline, and 2.85 g. of orange needles of the hydroxychloride obtained. The free base gives colorless needles from benzene, m. p. 181–183°.

Anal. Calcd. for $C_9H_7O_2N$: N, 8.70. Found: N, 9.01.

The sulfate gives orange needles from water and begins to decompose at 250°.

Hydroquinone.—Two grams of *p*-nitrosophenol was reduced in the way described above, except that the reaction mixture, on cooling, was directly shaken six times with ether. On evaporating the solvent, after decolorization with animal charcoal, 1 g. of light brown colored needles of hydroquinone was obtained, and recrystallized from hot water, m. p. 169–171°.

Anal. Calcd. for $C_6H_6O_2$: C, 65.45; H, 5.45. Found: C, 65.31; H, 5.46.

The mother liquor, after being made alkaline with sodium carbonate, was shaken six times with ether. On evaporating the solvent, 0.02 g. of almost colorless leaflets was obtained which after treatment with alcohol melted at 187–188°, and gave, in contact with calcium hypochlorite, color reactions specific to *p*-aminophenol.

Anal. Calcd. for C_6H_7ON: N, 12.84. Found: N, 12.94.

TABLE I

REDUCTION OF NITROPHENOL

Reactant	G.	Products	Yield, g.	M. p., and mixed m. p., °C.
p-Nitrophenol	2.8	Hydroquinone	0.45	169–170
		p-Aminophenol	.90	187
o-Nitrophenol	2.8	*o*-Aminophenol	1.65	179

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Summary

By reduction of nitrosophenols by iron and hydrochloric acid, the following compounds have been prepared: 5-acetyl-7,8-dihydroxyquinoline, 5,8-dihydroxyquinoline and hydroquinone.

TOKYO, JAPAN

[CONTRIBUTION FROM THE RESEARCH LABORATORY, CHEMISTRY DEPARTMENT, UNIVERSITY OF THE PHILIPPINES]

PHENOLIC DECOMPOSITION OF CERTAIN MIXED ETHERS. II. THE EFFECT OF SUBSTITUTION. THE RATE CONSTANT

BY D. M. BIROSEL

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In the first paper[1] of this series it was pointed out that the phenolic decomposition of mixed ethers is influenced by a number of factors. In the present investigation, the influence of substitution in the phenyl residue upon the decomposition of certain mixed ethers by hydrogen bromide in glacial acetic acid at the temperature of the steam-bath has been determined.

Experimental

Preparation of Materials.—When it was possible, the procedure adopted by Claisen[2] in preparing phenyl allyl ethers was followed to synthesize the mixed ethers used in this investigation. The scheme of procedure is

$$C_6H_5OH + C_3H_5I + K_2CO_3 \longrightarrow C_6H_5OC_3H_5 + KI + KHCO_3$$

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[1] Birosel, THIS JOURNAL, **52**, 1944 (1930).

[2] Claisen, *Ber.*, **45**, 3157 (1912); *Ann.*, **401**, 21 (1913); *ibid.*, **418**, 69 (1919).