

Hydrolysis of 7-Anilinobenzyl-8-quinolinol

By Motoko ITO

(Received August 21, 1959)

On heating with 4N hydrochloric acid 7-anilinobenzyl-8-quinolinol (I) gave 7-hydroxybenzyl-8-quinolinol (II) and aniline as major products. The formation of benzaldehyde was found to be very scanty at this reaction though a distinct odor of benzaldehyde was noticed, suggesting that dissociation into three components of the Mannich base proceeded only to a negligible extent. On further heating with hydrochloric acid, II produced neither 8-quinolinol nor benzaldehyde but gave undefined matter (m.p. 118~119°C, foaming at 125°C). The bromination of II produced 5,7-dibromo-8-quinolinol and benzaldehyde.

The dissociation of I by 4N hydrochloric acid was first studied by Phillips et al.¹⁾, however, it was considered at that time that I dissociated into three components in one step.

Experimental

7-Hydroxybenzyl-8-quinolinol (II).—A hot solution of I (0.5 g.) in 4N hydrochloric acid (10 ml.) was kept at around 85°C for 16 min. (when an odor of benzaldehyde was noticed). After being cooled, the solution was diluted with water (50 ml.) and then sodium acetate (6 g.) was added to it. The resulting precipitate was filtered after standing overnight (when no odor of benzaldehyde was noticeable). The filtrate gave a deep violet color with bleaching powder. The crude product was heated with ligroin (20 ml.) and filtered. From the filtrate on working up a colorless solid (0.15 g.), m.p. 88~100°C, foaming at 120~130°C, was isolated. This may be an impure bakelite-type condensation product.

The undissolved II was crystallized from five hundred times its weight of hot ligroin as colorless prismatic needles, m.p. 128°C.

Found: C, 76.52; H, 5.30; N, 5.20. Calcd. for $C_{16}H_{13}NO_2$: C, 76.49; H, 5.18; N, 5.58%.

When crystallized from benzene (20 ml.), it contained a mole of the solvent, m.p. 126~127°C; yield, 0.25 g. (66%) and when crystallized from carbon tetrachloride and dried in vacuo at room temperature, it also contained the solvent.

Found: C, 80.09; H, 5.65; N, 3.85. Calcd. for $C_{16}H_{13}NO_2 \cdot C_6H_6$: C, 80.24; H, 5.78; N, 4.26%.

Found: C, 53.84; H, 4.01. Calcd. for $C_{16}H_{13}NO_2 \cdot 0.8CCl_4$: C, 53.87; H, 3.47%.

The hydrochloride was obtained as colorless needles by the reaction of the base and hydrogen chloride, both in ethereal solution in the cold. It gave no definite m.p., began to sinter at 265°C and became a tar at 302°C.

Found: N, 4.73. Calcd. for $C_{16}H_{13}NO_2 \cdot HCl$: N, 4.87%.

The picrate was crystallized from benzene as prisms, m.p. 169°C.

Found: N, 11.50. Calcd. for $C_{16}H_{13}NO_2 \cdot C_6H_3N_3O_7$: N, 11.67%.

Acetyl Derivatives.—A mixture of II (0.2 g.), freshly fused sodium acetate (0.2 g.), acetic anhydride (0.4 ml.) and ether (20 ml.) was allowed to stand at room temperature for 3 days, ether was evaporated and then water was added to the reaction mixture. The resulting precipitate was filtered; yield, 0.26 g.

The crude product was treated with ether (50 ml.) and the undissolved solid was crystallized from benzene as thick plates, m.p. 135°C. Analysis proved it to be a monoacetyl compound. It gave no color reaction with ferric chloride. This suggests that phenolic hydroxyl was acetylated.

Found: C, 73.89; H, 4.89; N, 4.71. Calcd. for $C_{18}H_{15}NO_3$: C, 73.72; H, 5.12; N, 4.78%.

1) J. P. Phillips and A. L. Duckwall, *J. Am. Chem. Soc.*, **77**, 5505 (1955).

The crude product obtained from the ether extract by evaporating the solvent, was carefully recrystallized from ether as colorless prisms, m.p. 109~110°C. The analytical figures corresponded to those of the diacetyl derivatives.

Found: C, 71.49; H, 5.00; N, 4.06. Calcd. for $C_{20}H_{17}NO_4$: C, 71.64; H, 5.07; N, 4.18%.

II (m.p. 126~127°C) on heating with 4 N hydrochloric acid for 10 min. when no odor of benzaldehyde was noticed and further working gave a product m.p. 118~119°C foaming at 125°C.

5,7-Dibromo-8-quinolinol.—*Method A.*—A mixture of the Mannich base (I) (0.33 g., 0.001 mol.) and 4 N hydrochloric acid (7 ml.) was treated in the same manner as that of Phillips¹. The reaction mixture was neutralized with sodium acetate and the separated solid was filtered; yield, 0.65 g., m.p. 105~170°C. When it was crystallized from ethanol, it gave needles (0.17 g.) melting at 194~15°C alone or on admixture with a sample of 5,7-dibromo-8-quinolinol which was prepared by bromination of 8-quinolinol.

Method B.—To a mixture of II (0.33 g. 0.001 mol.) and 4 N hydrochloric acid (7 ml.) after it was diluted with water (50 ml.), one half normal bromate-bromide solution (8 ml.) was added dropwise.

After standing for 2 hr., the resulting solid (80 mg.) was filtered and crystallized from ethanol to give colorless needles, m.p. with a sample of 5,7-dibromo-8-quinolinol 194~195°C. A mixture of the filtrate of the crude product and an ethanolic solution of dinitro-phenylhydrazine (0.1 g.), on mild warming and long standing gave a solid, which crystallized from ethanol as orange elongated plates, m.p. 235~236.5°C and identified as benzaldehyde dinitrophenylhydrazone by mixed m.p. method.

The author wishes to thank Mr. Konomu Matsumura for help and advice throughout this work.

*Chemical Laboratory
Kitasato Institute
Minato-ku, Tokyo*