PROPERTIES OF 4-NITRO-3-HYDROXYQUINOLINE

K. M. Dyumaev and E. P. Popova

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It was found that the nitro group in 4-nitro-3-hydroxyquinoline readily undergoes exchange in acidic media; the corresponding 4-halo-, 4-mercapto, 4-phenylsulfonyl, and p-tolylthio derivatives of 3-hydroxyquinoline were obtained.

Unusual lability of the nitro group in 4-nitro-3-hydroxyquinoline (I) in acidic media was observed in an investigation of the properties of nitro derivatives of 3-hydroxyquinoline. Thus the corresponding 4-halo-3-hydroxyquinolines are formed smoothly on treatment of I with hydrochloric or hydrobromic acid.

However, we were unable to realize exchange of the nitro group in I under the usual conditions of nucleophilic substitution of a nitro group by an alkoxy or amino group, which proceeds in neutral or basic media. These facts make it possible to explain the ease of exchange of the nitro group by halogen as being due to the formation in acidic media of the 4-nitro-3-hydroxyquinolinium cation with reduced electron density on the $C_{(4)}$ carbon atom because of the mesomeric effect of the protonated ring nitrogen in addition to the inductive effect of the nitro group.

We attempted to prove the validity of this assumption by a number of experiments carried out in acidic media with various nucleophilic agents. Nucleophilic exchange was accomplished readily and in satisfactory yields with thiourea, benzenesulfinic acid, and p-thiocresol, but attempts to effect transformations with aniline, urea, and phenol were unsuccessful.

It should be noted that the anomalous lability of the nitro group in the quinoline series was previously observed in the case of 4-nitroquinoline N-oxide [1], which has a structure that is similar to the electronic structure of the protonated form of I.

EXPERIMENTAL

4-Phenylsulfonyl-3-hydroxyquinoline (II). A mixture of 0.38 g (2 mmole) of hydroxyquinoline I, 0.6 g (4 mmole) of benzenesulfinic acid, and 0.2 g (2 mmole) of sulfamic acid (III) was refluxed in 30 ml of water containing three drops of concentrated H_2SO_4 for 20 min until a precipitate began to form. The reaction mass was neutralized with ammonia, and the precipitate was removed by filtration, washed with water, and dried to give 0.47 g (84%) of II with mp 173.2° (from methanol). Found: C 63.2; H 3.7; N 4.5; S 10.9%. $C_{15}H_{11}NO_3S$. Calculated: C 63.1; H 3.5; N 4.9; S 11.2%.

4-Mercapto-3-hydroxyquinoline (IV). A mixture of 0.25 g (1.3 mmole) of I, 1 g (13 mmole) of thiourea, and 0.1 g (1 mmole) of III in 40 ml of water acidified with three drops of concentrated H_2SO_4 was held at room temperature for 3 days. The solution was then filtered, and the mother liquor was neutralized with ammonia and evaporated to 20-25 ml. The resulting precipitate was removed by filtration, washed with water, and dried to give 0.13 g (56.5%) of IV with mp 200-201° (from benzene). Found: C 61.0; H 4.0; N 8.0; S 18.1%. C_9H_7NOS. Calculated: C 61.0; H 4.0; N 7.9; S 18.1%.

4-(p-Tolylthio)-3-hydroxyquinoline (V). A mixture of 0.2 g (1 mmole) of I, 0.3 g (2.5 mmole) of p-thiocresol, and 0.1 g (1 mmole) of III in 30 ml of water acidified with

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concentrated H_2SO_4 was refluxed until a precipitate began to form. The mixture was then neutralized with ammonia, and the precipitate was removed by filtration and washed with water to give 0.1 g (38.5%) of V with mp 167.5° (from alcohol). Found: C 71.2; H 5.0; N 4.7; S 13.1%. $C_{16}H_{13}NOS$. Calculated: C 71.9; H 4.9; N 5.2; S 12.0%.

4-Chloro-3-hydroxyquinoline (VI). A mixture of 0.13 g (2.6 mmole) of I and 0.1 g (1 mmole) of III was refluxed in 20% HCl for 30 min, after which it was cooled and neutralized with 10% NaOH. The resulting precipitate was removed by filtration, washed with water, and dried to give a quantitative yield of VI with mp 199.2° (from aqueous alcohol). Found: C 60.2; H 3.2; Cl 19.3; N 7.8%. C_9H_6ClNO. Calculated: C 60.2; H 3.4; Cl 19.7; N 7.7%.

4-Bromo-3-hydroxyquinoline (VII). This compound, with mp 183° (from 50% aqueous alcohol), was obtained in quantitative yield by the method used to prepare VI with concentrated HBr in place of HCl. Found: C 48.9; H 2.9; Br 35.5; N 6.3%. C_9H_6BrNO. Calculated: C 48.2; H 2.7; Br 35.7; N 6.3%.

LITERATURE CITED

1. E. Ochiai, J. Org. Chem., 18, 534 (1953).