INVESTIGATION OF QUINOLINE DERIVATIVES

II.* DEHYDROGENATION OF MONONITRO-1,2,3,4-TETRAHYDROQUINOLINES

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The dehydrogenation of mononitro-1,2,3,4-tetrahydroquinolines and several of their N-acyl derivatives to the corresponding aminoquinolines was accomplished with various dehydrogenating agents. The maximum yields of aminoquinolines (15-20%) can be obtained when palladium on carbon is used as the dehydrogenating agent.

We have already reported [1] the possibility of the dehydrogenation of 6- and 7-nitro-1,2,3,4-tetrahydroquinolines (THQ) with chloranil and a copper–pyridine complex to the corresponding nitro derivatives of quinoline. The present communication is devoted to the dehydrogenation of the same 6- and 7-nitro-THQ and several of their N-acyl derivatives, which is accompanied by simultaneous reduction of the nitro group and leads to the formation of the corresponding aminoquinolines.

Two types of dehydrogenating agents were investigated: 1) substances that change their valence state during the reaction – ferric sulfate (concentrated H_2SO_4, 120-130°C),‡ hydrogen peroxide and silver nitrate (concentrated H_2SO_4, 60-70°), cupric acetate (methanol, ethanol), sulfur (molten, 140-160°; concentrated H_2SO_4, 100-130°; p-xylene) potassium dichromate (concentrated H_2SO_4, 100-120°), and cupric chloride (p-xylene) – 2) catalysts – palladium on carbon (p-xylene), palladium on calcium carbonate (p-xylene), palladium on carbon and cinnamic acid (p-xylene), and a nickel–paraffin catalyst (paraffin, 110-140°).

As a rule, the use of the dehydrogenating agents of the first group leads to low yields of the dehydrogenation products, which could be ascertained only qualitatively by means of thin-layer chromatography on a loose layer of aluminum oxide. The dehydrogenation of N-acyl derivatives of mononitro-THQ is accomplished only in the presence of sulfuric acid, which apparently makes the dehydrogenation possible as a consequence of hydrolysis and formation of a free base.

Tafel [2] and Rugin and Morard [3] used mercuric acetate for the dehydrogenation of 6-acetyl- and 8-carboxy-THQ. In an attempt to use this dehydrogenating agent for 7-nitro-THQ, a colored reaction product was isolated. According to elementary analysis, this colored product was 7-nitro-N-acetylmercuri-THQ, which readily undergoes acid hydrolysis to form the starting 7-nitro-THQ.

Catalytic dehydrogenation with simultaneous reduction of the nitro group is also known in the THQ-analogous indoline series. The dehydrogenation of 5-nitroindoline in the presence of Raney nickel gives 50% 5-aminoindoles [4, 5]. We noted the similar reduction of the nitro group during the dehydrogenation of 7-nitro-THQ by palladium on carbon. In this case, the maximum yield of aminoquinoline is 15-20%.

Nickel formate was also investigated as a dehydrogenating agent under the following conditions: fused, 240-260°; acetamide, 222°; naphthalene, 218°; tetralin, 207.5°; paraffin, 240-260°. Dehydrogena-

*See [1] for communication I.

†Deceased.

‡Here and elsewhere, the solvent and reaction temperature are indicated in parentheses; if the temperature is not stipulated, the reaction was carried out by refluxing the reaction mass.

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tion to give 6% aminoquinoline occurred at 240-260°, i.e., at the temperature interval of the decomposition of nickel formate:

$$Ni(HCOO)_2 \cdot 2H_2O \longrightarrow Ni + 3H_2O + CO + CO_2 .$$

EXPERIMENTAL

Dehydrogenation of 7-Nitro-THQ by Mercuric Acetate to Give 7-Nitro-N-acetylmercuri-THQ. A mixture of 0.18 g (0.001 mole) of 7-nitro-THQ in 30 ml of absolute ethanol and 1.9 g (0.006 mole) of mercuric acid was refluxed for 5 h. The hot solution was filtered, and the filtrate was cooled to give 0.43 g (95%) of shiny, crimson-colored crystals that decomposed above 250°. Found: C 20.3; 20.1; H 2.4; 2.2%. $C_{11}H_{12}HgN_2O_4$. Calculated: C 20.2; H 2.7%.

Dehydrogenation of 7-Nitro-THQ in the Presence of Palladium on Carbon. A mixture of 1.8 g (0.01 mole) of 7-nitro-THQ and 0.5 g of palladium on carbon [6] in 50 ml of dry p-xylene was refluxed for 25 h and cooled. The catalyst was removed by filtration and placed in a Soxhlet apparatus. The reaction products were extracted with ethanol for 3 h. The alcohol extract was combined with the xylene filtrate, and the solvents were vacuum evaporated. 7-Aminoquinoline was isolated by means of preparative thin-layer chromatography on 10-15 plates on activity III aluminum oxide (Brockmann classification) in a chloroform-concentrated ammonium hydroxide system (2:1). The eluent was ethanol and the yield of product with mp 74-75° [7] and R_f 0.04 was 0.26 g (18%).

7-Acetamidoquinoline. This compound was obtained as colorless crystals with mp 166-167° and R_f 0.03. Found: C 70.8; 71.0; H 5.4; 5.4%. $C_{11}H_{10}N_2O$. Calculated: C 70.9; H 5.4%.

7-(o-Hydroxybenzylideneamino)quinoline. This compound was obtained as yellow crystals with mp 161-161.5° and R_f 0.05. Found: C 77.6; 77.7; H 4.7; 5.0%. $C_{17}H_{12}N_2O$. Calculated: C 78.4; H 5.0%.

6-Aminoquinoline. This compound was similarly prepared to give 0.29 g (20%) of a product with mp 118° (from ethanol) [8] and R_f 0.05.

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