

INVESTIGATION OF THE PRODUCTS OF THE REACTION OF EPICHLOROHYDRIN WITH AROMATIC AMINES

VIII.* SYNTHESIS AND INVESTIGATION

OF 3-HYDROXY-1,2,3,4-TETRAHYDROBENZO[f]QUINOLINE DERIVATIVES

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5,6-Dichlorobenzo[f]quinoline is formed by the action of thionyl chloride on 3-hydroxy-5-chloro-1,2,3,4-tetrahydrobenzo[f]quinoline hydrochloride. 7-Chlorobenzo[f]quinoline and 7-chloro-1,2,3,4-tetrahydrobenzo[f]quinoline are obtained in good yields by heating 3-hydroxy-7-chloro-1,2,3,4-tetrahydrobenzo[f]quinoline with orthophosphoric acid, while benzo[f]quinoline is also obtained by heating it with polyphosphoric acid.

In a continuation of our investigations [2-6] we have studied the reaction of thionyl chloride with 3-hydroxy-5-chloro-1,2,3,4-tetrahydrobenzo[f]quinoline hydrochloride (I). The latter was obtained either by heating 3-chloro-1-naphthylamine (II) with epichlorohydrin or by heating N-(3-chloro-2-hydroxypropyl)-3-chloro-1-naphthylamine (III) in chlorobenzene at 150-155°. The formation of a benzoic acid ester and N-benzoyl-3-hydroxy-5-chloro-1,2,3,4-tetrahydrobenzo[f]quinoline (IV) may serve as a confirmation of structure I. Treatment of I with thionyl chloride at 75-80° leads not only to aromatization of the tetrahydropyridine ring but also to chlorination of I to form 5,6-dichlorobenzo[f]quinoline (V). Consequently, the introduction of a methyl group [4] as well as a chlorine atom into the 5 position of I does not hinder chlorination.

N-Mono or N,N-bis(2,3-epoxypropyl) derivatives of aromatic amines are used to dye natural and chemical fibers [7-10]. N-(2,3-Epoxypropyl) derivatives of 1,2,3,4-tetrahydrobenzo[f]quinoline [11] are used to obtain darker dyes, but the photostability of such dyes is low. In order to increase the photostability of the dyes we have synthesized N-(2,3-epoxypropyl)-5-chloro-1,2,3,4-tetrahydrobenzo[f]quinoline (VI) and N-(2,3-epoxypropyl)-7-chloro-1,2,3,4-tetrahydrobenzo[f]quinoline (VII). For the synthesis of VI, 5-chlorobenzo[f]quinoline (VIII) was obtained by the Skraup method from II and was then reduced to 5-chloro-1,2,3,4-tetrahydrobenzo[f]quinoline (IX). Heating of IX with epichlorohydrin gives N-(3-chloro-2-hydroxypropyl)-5-chloro-1,2,3,4-tetrahydrobenzo[f]quinoline (X), which was converted to VI by treatment with aqueous sodium hydroxide. The reaction of 3-hydroxy-7-chloro-1,2,3,4-tetrahydrobenzo[f]quinoline (XI) with polyphosphoric acid or orthophosphoric acid was investigated to obtain VII. As was demonstrated in [1], benzo[f]quinoline and its 1,2,3,4-tetrahydro derivative are obtained in good yields when 3-hydroxy-1,2,3,4-tetrahydrobenzo[f]quinoline is heated with polyphosphoric or orthophosphoric acid; it could therefore be assumed that 7-chlorobenzo[f]quinoline (XII) and 7-chloro-1,2,3,4-tetrahydrobenzo[f]quinoline (XIII) would form when XI was heated with the indicated acids.

*See [1] for communication VII.

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was filtered and dissolved in 30 ml of alcohol. The alcohol solution was made alkaline with 25% sodium hydroxide and diluted with 30 ml of water. The resulting precipitate was filtered and recrystallized from alcohol to give 0.6 g (49%) of V with mp 147–148.5°. Found %: Cl 28.2, 28.3. $C_{13}H_7Cl_2N$. Calc. %: Cl 28.5.

5-Chlorobenzo[f]quinoline (VIII). This compound was obtained via the Skraup method [12] and had mp 110.5–111.5° (from alcohol). Found %: Cl 16.2, 15.9. $C_{13}H_8ClN$. Calc. %: Cl 16.3.

Picrate of 5-Chloro-1,2,3,4-tetrahydrobenzo[f]quinoline (IX). A mixture of 1.6 g (0.007 mole) of VIII, 5.0 g of tin, and 25 ml of concentrated hydrochloric acid was refluxed at 140–145° for 25 h. The resulting precipitate was filtered, treated with aqueous sodium hydroxide, and extracted with ether. After removal of the solvent, the oily substance was dissolved in 50 ml of alcohol and mixed with a solution of 1.4 g (0.007 mole) of picric acid in alcohol. The resulting precipitate was filtered and recrystallized from alcohol to give 1.5 g (46%) of the picrate of IX with mp 142° (dec.). Found %: N 12.3, 12.6. $C_{13}H_{12}ClN \cdot C_6H_3N_3O_7$. Calc. %: N 12.5.

N-(3-Chloro-2-hydroxypropyl)-5-chloro-1,2,3,4-tetrahydrobenzo[f]quinoline (X). A mixture of 3.2 g (0.015 mole) of VIII, 10.0 g of tin, and 50 ml of concentrated hydrochloric acid was refluxed at 140–145° for 25 h. The subsequent workup was the same as indicated for the preparation of IX. A mixture of 2.2 g of the oily substance obtained, 1.4 g of epichlorohydrin, and 0.8 g of glacial acetic acid was heated at 45–50° for 3 days. After cooling, the resulting precipitate was filtered, washed with acetic acid, and recrystallized from alcohol to give 2.0 g (66%) of X with mp 119–120°. Found %: Cl 22.6, 22.5. $C_{16}H_{17}Cl_2NO$. Calc. %: Cl 22.9.

N-(2,3-Epoxypropyl)-5-chloro-1,2,3,4-tetrahydrobenzo[f]quinoline (VI). X [1.2 g (0.004 mole)] was dissolved in 30 ml of absolute ether, 0.2 g (0.02 mole) of pulverized sodium hydroxide was added, and the mixture was heated at 40–45° for 3 h. The mixture was then washed with water until it no longer gave a reaction for chloride and hydroxyl ions. After removal of the ether by distillation, the residue was recrystallized from methanol to give 0.7 g (64%) of VI with mp 81–82°. Found %: Cl 12.7, 13.0. $C_{16}H_{10}ClNO$. Calc. %: Cl 12.9.

Reaction of 3-Hydroxy-7-chloro-1,2,3,4-tetrahydrobenzo[f]quinoline (XI) with Orthophosphoric Acid. A mixture of 4.7 g (0.02 mole) of XI and 20 ml of orthophosphoric acid was heated at 200–205° for 1.5 h. The reaction mass was poured into 200 ml of water, and the mixture was neutralized with 25% aqueous NaOH and extracted with ether. After removal of the solvent, the residue was dissolved in 30 ml of absolute ether, 3.0 g of potassium carbonate and 1.5 g of benzoyl chloride were added, and the mixture was refluxed for 4 h. The precipitate was filtered, washed with water, and recrystallized from alcohol to give 1.4 g (34%) of XVI with mp 172–173°. Found %: Cl 11.1, 11.3. $C_{20}H_{16}ClNO$. Calc. %: Cl 11.1. This product did not depress the melting point of XVI obtained by benzoylation of pure XIII.

The ether filtrate after removal of the crystals of XVI was washed with water and aqueous sodium carbonate. The ether was removed by distillation, and the residue was recrystallized from alcohol to give 1.0 g (25%) of XII with mp 100–101°. Found %: Cl 16.6, 16.4. $C_{13}H_8ClN$. Calc. %: Cl 16.6.

Reaction of 3-Hydroxy-7-chloro-1,2,3,4-tetrahydrobenzo[f]quinoline (XI) with Polyphosphoric Acid. A mixture of 10.0 g (0.04 mole) of XI and 40 ml of polyphosphoric acid was heated at 200–205° for 1.5 h. The mass was then poured into 500 ml of water, and the mixture was neutralized with 25% aqueous NaOH and extracted with ether. After removal of the solvent, the oily residual substance was vacuum-distilled and then subjected to fractional crystallization from alcohol and petroleum ether to give 1.1 g (13%) of XIII with mp 65.5–66.5°. Found %: Cl 16.4, 16.6; N 6.1, 6.0. $C_{13}H_{12}ClN$. Calc. %: Cl 16.3; N 6.4. This product did not depress the melting point of XIII obtained by reduction of XII [13]. Also obtained were 1.3 g (15%) of XII with mp 100–101° (did not depress the melting point of XII obtained in the previous experiment and via the Skraup method from 5-chloro-1-naphthylamine [12]) and 0.3 g (4%) of XIV with mp 51–52° [12].

N-(3-Chloro-3-hydroxypropyl)-7-chloro-1,2,3,4-tetrahydrobenzo[f]quinoline (XVII). A mixture of 1.5 g (0.006 mole) of XIII, 0.8 g (0.009 mole) of epichlorohydrin, and 0.8 g of glacial acetic acid was heated at 40–50° for 3 days. The resulting precipitate was filtered, washed with acetic acid, and recrystallized from alcohol to give 1.3 g (72%) of XVII with mp 97–98°. Found %: Cl 22.9, 22.7. $C_{16}H_{17}Cl_2NO$. Calc. %: Cl 22.9.

N-(2,3-Epoxypropyl)-7-chloro-1,2,3,4-tetrahydrobenzo[f]quinoline (VII). XVII [1.5 g (0.005 mole)] was dissolved in 30 ml of absolute ether, 0.8 g (0.02 mole) of pulverized sodium hydroxide was added, and the mixture was refluxed for 3 h. The reaction mixture was washed with water until it no longer gave a

reaction for chloride and hydroxyl ions. After removal of the ether by distillation, the residue was vacuum-distilled under nitrogen to give 1.0 g (71%) of a fraction with bp 185-186° (2 mm). Found %: Cl 13.2, 13.2; N 4.8, 4.7. $C_{15}H_{16}ClNO$. Calc. %: Cl 13.0; N 5.1.

LITERATURE CITED

1. S. I. Kutkevichus and K. S. Sherenas, *Khim. Geterotsikl. Soedin.*, 1526 (1970).
2. N. N. Vorozhtsov, Jr., and S. I. Kutkevichus, *Zh. Obshch. Khim.*, 28, 2682 (1958).
3. B. I. Milukas, S. I. Kutkevichus, and N. N. Vorozhtsov, Jr., *Khim. Geterotsikl. Soedin.*, 554 (1965).
4. S. I. Kutkevichus, B. I. Milukas, and N. N. Vorozhtsov, Jr., *Khim. Geterotsikl. Soedin.*, No. 1, 300 (1967).
5. S. I. Kutkevichus and R. I. Valite, *Khim. Geterotsikl. Soedin.*, 969 (1970).
6. S. I. Kutkevichus and R. I. Shablinskas, *Khim. Geterotsikl. Soedin.*, 1522 (1970).
7. S. I. Kutkevichus, Yu. I. Lakshtauskas, and M. R. Pesite, USSR Author's Certificate No. 165,669 (1964); *Byull. Izobr.*, No. 20, 6 (1964).
8. S. I. Kutkevichus, Yu. I. Lakshtauskas, and S. I. Rutkauskas, USSR Author's Certificate No. 173,708 (1965); *Byull. Izobr.*, No. 16, 21 (1965).
9. S. I. Kutkevichus and Yu. I. Lakshtauskas, USSR Author's Certificate No. 180,170 (1966); *Byull. Izobr.*, No. 7, 10 (1966).
10. S. I. Kutkevichus, Yu. I. Lakshtauskas, and M. R. Pesite, USSR Author's Certificate No. 215,398 (1968); *Byull. Izobr.*, No. 13, 59 (1968).
11. S. I. Kutkevichus, Yu. I. Lakshtauskas, and M. R. Pesite, *Nauchn. Trudy Vuzov Lit. SSR, Khim. i Khim. Tekhnol.*, 7, 53 (1965).
12. Z. H. Skraup, *Monatsh.*, 2, 163 (1881).
13. E. Bamberger and L. Stettenheimer, *Ber.*, 24, 2475, 2476 (1891).