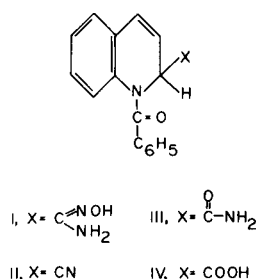


## Reaction of Hydroxylamine with a Reissert Compound

Lee R. Walters, Marvin I. Siegel (1) and Robert C. Cook (1)

Department of Chemistry, Lafayette College

1-Benzoyl-1,2-dihydroquinaldamidoxime (I) was obtained in excellent yield by the reaction of 1-benzoyl-1,2-dihydroquinaldonitrile (II) with hydroxylamine in a manner analogous to that previously described for the reaction of 1-benzoyl-6-methoxy-1,2-dihydroquinaldonitrile with hydroxylamine (2).



Hydrolysis of I with 10% aqueous hydrochloric acid led to an unusual result in that benzaldehyde was obtained in 38% yield along with benzoic acid, quinoline and quinaldic acid. These results are similar to the unusual acid-catalyzed hydrolysis of 1-benzoyl-1,2-dihydroquinaldonitrile (II) which gives benzaldehyde in excellent yield along with quinaldic acid and a small amount of quinaldamide (3,4).

The acid-catalyzed hydrolysis of I might be expected to lead to the rapid formation of 1-benzoyl-1,2-dihydroquinaldamide (III) as acidic hydrolysis rapidly converts amidoximes to amides and hydroxylamine (5). However, continued acid-catalyzed hydrolysis does not convert III to the corresponding acid (IV) but gives benzoic acid and no trace of benzaldehyde (3). In order to obtain benzaldehyde from 1-benzoyl-1,2-dihydroquinaldamide (III), it must first be treated with a dehydrating agent such as polyphosphoric acid and then hydrolyzed (6). Thus, after the initial solution of I in 10% hydrochloric acid, the mechanism of hydrolysis by which benzaldehyde is formed must be similar to that proposed by Cobb and McEwen for the hydrolysis of Reissert compounds (3).

Hydrolysis of I with concentrated hydrochloric acid in the presence of 2,4-dinitrophenylhydrazine gave a 79% yield of benzaldehyde, isolated as the 2,4-dinitrophenyl-

hydrazone, and a 55% yield of quinaldic acid along with smaller amounts of benzoic acid and quinoline.

## EXPERIMENTAL (7)

## 1-Benzoyl-1,2-dihydroquinaldamidoxime (I).

To a solution of 10.0 g. (0.04 mole) of 1-benzoyl-1,2-dihydroquinaldonitrile (8) in warm methanol was added dropwise an ice-cold methanol solution of hydroxylamine. The hydroxylamine solution was prepared by mixing a solution of 4.2 g. hydroxylamine hydrochloride in 25 ml. of methanol with a solution containing 1.4 g. of sodium in 25 ml. of methanol and removing the precipitated sodium chloride. After stirring for 1 hour at room temperature, the reaction mixture was cooled and filtered to give 10.95 g. (94.0%) of I. Recrystallization from *N,N*-dimethylformamide-water (4:3) gave a white crystalline solid, m.p. 176-177°. The infrared spectrum (potassium bromide pellet, 1.5 mg./300 mg.) shows a doublet at 2.92  $\mu$  and 3.01  $\mu$  and a broad band having a maximum at 3.14  $\mu$  (9).

*Anal.* Calcd. for  $\text{C}_{17}\text{H}_{15}\text{N}_3\text{O}_2$ : C, 69.62; H, 5.17; N, 14.33. Found: C, 69.49; H, 5.21; N, 14.18.

For the subsequent hydrolysis reactions, each sample of I was recrystallized several times to a constant melting point of 176-177°. A thin layer chromatogram of I on Eastman Chromagram Sheet (Type K 301 R) developed with benzene-acetic acid (8:7) at room temperature showed only a singlet spot upon exposure to ultraviolet light. Compounds I and II had  $R_f$  values of 0.50 and 0.67, respectively, under similar conditions.

## Hydrolysis of I Using 10% Hydrochloric Acid.

Three grams (0.01 mole) of I was dissolved in 200 ml. of 10% hydrochloric acid and the solution refluxed for two hours. The reaction mixture was then steam distilled and the distillate extracted with ether. Concentration of the dried ether followed by reaction with 2,4-dinitrophenylhydrazine gave 1.12 g. (38.2%) of benzaldehyde 2,4-dinitrophenylhydrazone, m.p. 237-239°.

The acidic steam distillation residue gave 0.71 g. (56.8%) of benzoic acid, m.p. 120-121° and upon being made basic gave 0.55 g. (41.6%) of quinoline which was characterized as its picrate, m.p. 201-203°.

The remaining aqueous residue was made faintly acid with acetic acid and a hot saturated solution of copper sulfate added. The blue-green precipitate which formed was filtered, washed and decomposed with hydrogen sulfide. The copper sulfide was filtered and washed with hot water. Evaporation of the combined filtrates gave 0.63 g. (35.6%) of quinaldic acid, m.p. 156-157°.

## Hydrolysis of I Using Concentrated Hydrochloric Acid.

A mixture of 3.0 g. of I, 2.3 g. of 2,4-dinitrophenylhydrazine and 125 ml. of concentrated hydrochloric acid was heated under reflux for six hours and allowed to stand overnight (3). An

additional 400 ml. of water was added, the mixture heated on a steam bath and the insoluble orange precipitate removed to give 2.30 g. (78.5%) of benzaldehyde 2,4-dinitrophenylhydrazone, m.p. 237-238°. The filtrate was made basic with sodium bicarbonate and the precipitated 2,4-dinitrophenylhydrazine removed. The filtrate yielded 0.17 g. (13.6%) benzoic acid, 0.22 g. (16.9%) quinoline and 0.97 g. (54.8%) quinaldic acid.

Acknowledgment.

We wish to thank the National Science Foundation Undergraduate Research Participation Program for support of this work.

#### REFERENCES

(1) Participants in National Science Foundation Undergraduate Research Participation Program.

(2) A. Gassmann and H. Rupe, *Helv. Chim. Acta*, **22**, 1241 (1939).

(3) R. L. Cobb and W. E. McEwen, *J. Am. Chem. Soc.*, **77**, 5042 (1955).

(4) A. Reissert, *Ber.*, **38**, 1603 (1905).

(5) F. Tiemann, *ibid.*, **18**, 1060 (1885).

(6) R. F. Collins and T. Henshall, *J. Am. Chem. Soc.*, **80**, 159 (1958).

(7) All melting points were taken in capillaries and are corrected. Analysis by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

(8) H. Rupe, R. Paltzer and K. Engel, *Helv. Chim. Acta*, **20**, 209 (1937).

(9) F. Eloy and R. Lenaers, *Chem. Rev.*, **62**, 155 (1962). Ref. 36a contained therein as unpublished results of F. Eloy and R. Lenaers notes that the infrared spectra of amidoximes show a doublet at 2.87-2.93  $\mu$  and 2.96-3.03  $\mu$  and a very broad band with a maximum at approximately 3.2  $\mu$ .

Received September 13, 1967

Easton, Pa. 18042