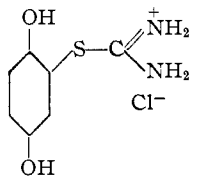
only small amounts of the derivative, I, are produced.

Dimroth, Kraft and Aichinger[3] described bis and trisphenylthioquinones and accounted for their formation by the first steps of the scheme above. I seems to be the first tetrathio derivative to be reported.

Thiourea also reacts with quinone in aqueous medium and at room temperature producing dark colored products which could not be crystallized. However, by working in acid medium and keeping to temperatures not above 30° even during recrystallization procedures, white crystalline products have been obtained. These are salts of the base 2,5-dihydroxyphenyl isothiourea. The hydrochloride is



II

The sulfate is less soluble and the nitrate is quite insoluble in cold water. In hot water these salts rapidly decompose forming reddish tars. The free base crystallizes out on neutralization of an aqueous solution of the chloride. Nitric acid oxidizes them to a red compound but this has not been isolated. A similar thiouronium salt has been isolated from 2-methylnaphthoquinone, differing, however, in that a mole of water has been split out. This compound is even less stable than II.

Experimental

Hydroquinone Tetrathioglycolic Acid.—Powdered *p*-benzoquinone (50 g.) was suspended in water (400 ml.). The suspension was stirred and a solution of thioglycolic acid (36 ml. or 48 g.) in water (150 ml.) was added dropwise over two and one-half hours. The mixture at first turned to a dark brown suspension and finally to a light brown solution from which a white crystalline product separated. The mixture was stirred until no more dark particles were left, a total of three hours. It was then chilled and the white crystalline product filtered off. It was recrystallized from 1500 ml. of boiling water by chilling; yield 14 to 17 g.; m. p. 288 to 289° with decomposition. For analysis it was recrystallized twice more.

Anal. Calcd. for $C_{14}H_{14}O_{10}S_4$: C, 35.75; H, 3.00; S, 27.23. Found: C, 35.96; H, 3.12; S, 27.44.

This compound dissolved in water on addition of sodium bicarbonate and such a solution was slowly oxidized by air to a deep red quinone.

Hydroquinone was recovered from the filtrate of the reaction mixture by evaporating *in vacuo* to 250 ml., adding 25 g. of sodium bicarbonate and extracting five times with 200-ml. portions of ether. Drying and evaporating the ether left a crystalline residue (37 g.) which on recrystallization from water gave a product (24 g.) with a melting point and mixed melting point with hydroquinone of 171°.

Chloranil (10 g.) stirred in water (100 ml.) was heated in a bath at 100° while thioglycolic acid (45 cc.) was added dropwise over a half hour. A thick suspension of white crystals remained which was chilled and filtered. The product was recrystallized as above and 16.8 g. or 83% was obtained with m. p. 288 to 289° with decomposition. Mixed melting point of the two preparations was also 288 to 289°.

Anal. Found: C, 35.56; H, 3.11; S, 27.21.

Hydroquinone tetrathioglycolic acid (15 g.) was added to a mixture of water (1000 ml.) and concentrated nitric acid (200 ml.) in a bath at 50 to 60° and stirred for fifteen minutes. A red crystalline product was formed. After chilling it was filtered off, washed with water and extracted with boiling water (1800 ml.). The clear red solution was filtered and cooled. The red crystalline product was filtered off within an hour and dried; yield 9 g. After one more recrystallization from water, the m. p. was 270 to 273° with decomposition.

Anal. Calcd. for $C_{14}H_{12}O_{10}S_4$: C, 35.90; H, 2.58; S, 27.35. Found: C, 35.71; H, 3.11; S, 27.59.

This quinone on reduction in hot water with aqueous thioglycolic acid gave the corresponding hydroquinone I, in a yield of 90% after recrystallization.

2,5-Dihydroxyphenylthiouronium Chloride.—Quinone (32 g.) was powdered and added in portions over fifteen minutes with good stirring to thiourea (30 g.) in 2 *M* hydrochloric acid (150 ml.). A white crystalline product separated. Concentrated hydrochloric acid (25 ml.) was added and the mixture chilled. The product was dissolved in water (325 ml.) at room temperature, stirred with Darco (2 g.), filtered and the product precipitated by addition of concentrated hydrochloric acid (70 ml.) and chilling; yield 40 g. or 60% of the theoretical. The compound decomposed on heating between 150 and 160°.

Anal. Calcd. for $C_7H_9O_2SN_2Cl$: C, 38.18; H, 4.12; S, 14.54; N, 12.76; Cl, 16.14. Found: C, 38.71; H, 4.27; S, 14.63; N, 12.15; Cl, 16.07.

Thiourea reacted similarly with 2-methylnaphthoquinone to give a product with salt-like character that was very unstable in hot water. A mixture of 2-methylnaphthoquinone (0.5 g.), thiourea (1.5 g.), 2 *M* hydrochloric acid (20 ml.) and alcohol (5 ml.) was stirred for two hours. The mixture at first turned brown then pale yellow and became perfectly clear. After a few days on ice, more rapidly on seeding, a white crystalline product separated. It was recrystallized by dissolving in water (35 ml.) and precipitating by addition of concentrated hydrochloric acid (10 ml.). A yield of 0.4 to 0.5 g. resulted.

Anal. Calcd. for $C_{12}H_{11}ON_2SCl$: C, 54.15; H, 4.16; N, 10.53; S, 12.03; Cl, 13.35. Found: C, 53.77; H, 4.81; N, 10.58; S, 12.06; Cl, 13.53.

The compound had no melting point but turned gray on heating over 260°.

DEPARTMENT OF THERAPEUTICS
NEW YORK UNIVERSITY COLLEGE OF MEDICINE
NEW YORK, N. Y. RECEIVED NOVEMBER 6, 1946

(3) Dimroth, Kraft and Aichinger, *Ann.*, **545**, 124 (1940).

A Convenient Synthesis of β-Chloropropionitrile

BY ROSS STEWART AND R. H. CLARK

Having occasion to use considerable quantities of β-chloropropionitrile the present authors have investigated a new method for its synthesis, the usual method being treatment of ethylene cyanohydrin with phosphorus pentachloride.[1] This compound, however, can be synthesized very conveniently and in good yield by the addition of 0.95 equivalent of dry hydrogen chloride gas to the cheap and readily obtainable acrylonitrile.

An excess of hydrogen chloride lowers the yield because of the production of β-chloropropionimide chloride.

$$ClCH_2CH_2CN + HCl \longrightarrow ClCH_2CH_2CCl{=}NH$$

That the product is β-chloropropionitrile and not the α-chloro isomer, is shown by the agreement of the density figure ($d^{18.4}_4$ 1.1443) with that in the literature.[1]

Procedure

Dry hydrogen chloride gas is bubbled rapidly into 2 moles (106 g.) of acrylonitrile (Eastman Kodak Co., Practical) cooled in an ice-bath. The dry gas is rapidly absorbed and the reaction vessel may be removed from the ice-bath and weighed with the gas passing through. After the weight has increased by 69 g. the clear mixture is distilled (68–71° at 16 mm.), washed with 10% sodium carbonate solution, and dried over anhydrous sodium sulfate. On redistillation the fraction boiling at 70–71° at 16 mm. yields 144 g. of pure product, (80%).

(1) L. Henry, *Bull. acad. roy. med. Belg.*, (3) **35**, 360 (1898).

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF BRITISH COLUMBIA
VANCOUVER, B. C. RECEIVED DECEMBER 10, 1946

Phenyl-pyridylhydantoins

BY PEYTON C. TEAGUE

A recent paper on diquinolylhydantoin[1] prompts this report on the preparation of the first two members of a series of similar compounds which are being prepared in this Laboratory. 5-Phenyl-5-(α-pyridyl)-hydantoin and 5-phenyl-5-(γ-pyridyl)-hydantoin have been prepared as examples of analogs of 5,5-diphenylhydantoin having a basic heterocyclic substituent.

A mixture of α- and γ-benzylpyridines was prepared by the method of Chichibabin.[2] The isomers were separated as their picrates by a modification of the method of LaForge.[3] The benzylpyridines, liberated from their picrates, were oxidized to the corresponding benzoylpyridines. These ketones were converted to the hydantoins by a modification of Bucherer's reaction.[4]

Experimental[5]

Separation of α- and γ-Benzylpyridines.—The benzylpyridine mixture prepared by the method of Chichibabin[2] and separated from most of the impurities by the method of LaForge[3] was converted to the picrates. It was found that the picrates could be isolated in the pure state by a combination of crystallization and mechanical separation. Slow crystallization from acetone produced large prisms of the α-compound together with very fine crystals of the γ-compound. The mixture was stirred with a quantity of boiling methanol insufficient for complete solution, and the methanol was decanted off. Several repetitions of this methanol treatment removed practically all of the γ-compound, partly in solution and partly in suspension. The crude γ-fraction was evaporated to dryness and the acetone recrystallization and methanol decantation repeated many times. The γ-benzylpyridine picrate was freed from the last traces of the α-compound by recrystallization from methanol; m. p. 141–142°. The collected residues of the α-benzylpyridine picrate were finally obtained pure by recrystallization from acetone; m. p. 141.5–142°. A mixture of the two melted at 117–130°. The free benzylpyridines were recovered from the picrates by suspending in hot water and treating with ammonia. The α-isomer boiled at 275–276° and the γ-isomer at 285–286° at 750 mm.

Preparation of α- and γ-Benzoylpyridines.—Each of the benzylpyridines was dissolved in aqueous sulfuric acid solution and heated to 100°. A 10% solution of potassium permanganate containing twice the calculated amount was added slowly with stirring, and the mixture was kept at approximately 100° for three to four hours. The mixture was made alkaline with sodium hydroxide and extracted with ether. The ether solution was dried over anhydrous sodium sulfate and the ether evaporated off. The γ-benzoylpyridine was recrystallized from petroleum ether; m. p. 72°; picrate m. p. 160°. The α-benzoylpyridine was distilled; b. p. 315–319° at 750 mm.; picrate m. p. 128–129°. These values are in agreement with those reported by previous workers.[3,6] Hydantoin preparations with the unpurified products were also satisfactory in both cases.

5-Phenyl-5-α-(and γ-)-pyridylhydantoin.—The procedure of Henze and Speer[7] for conversion of ketones into hydantoins was used except that the mixture was heated for forty-eight hours instead of two hours. To purify the products, the reaction mixture was made acid with hydrochloric acid until the precipitate which formed had redissolved. The solution was filtered and sodium hydroxide added until the precipitate again formed and redissolved. The alkaline mixture was extracted with ether and the ether discarded. An excess of acid was then added, the solution made exactly neutral with sodium bicarbonate and the hydantoin was filtered off, dried and recrystallized from chloroform.

5-Phenyl-5-(α-pyridyl)-hydantoin; yield 77%, m. p. 237.5–238°. *Anal.* Calcd. for $C_{14}H_{11}N_3O_2$: C, 66.39; H, 4.38. Found: C, 66.59; H, 4.30.

5-Phenyl-5-(γ-pyridyl)-hydantoin; yield 63%, m. p. 253–255°. *Anal.* Calcd. for $C_{14}H_{11}N_3O_2$: C, 66.39; H, 4.38. Found: C, 66.34; H, 4.60.

(1) Linsker and Evans, THIS JOURNAL, **68**, 947 (1946).

(2) A. E. Chichibabin, *J. Russ. Phys.-Chem. Soc.*, **33**, 249 (1901); **47**, 1297 (1915), from *Chem. Zentr.*, **72**, II, 127 (1901); **87**, II, 146 (1915).

(3) F. B. LaForge, THIS JOURNAL, **50**, 2484 (1928).

(4) Bucherer and Lieb, *J. prakt. Chem.*, **141**, 5 (1934).

(5) All melting points and boiling points are corrected.

(6) A. E. Chichibabin, *J. Russ. Phys.-Chem. Soc.*, **33**, 700 (1901), from *Chem. Zentr.*, **73**, I, 206 (1902).

(7) Henze and Speer, THIS JOURNAL, **64**, 522 (1942).

DEPARTMENT OF CHEMISTRY
THE UNIVERSITY OF GEORGIA
ATHENS, GEORGIA RECEIVED AUGUST 26, 1946

3,4-Dihydro-3-keto-4,6,7-trimethyl-2-quinoxalinecarboxylic Acid

BY J. W. WELLMAN[1] AND MAX TISHLER

In the alkaline degradation of lumiflavin, 7,8,10-trimethylisoalloxazine, Kuhn and collaborators[2] isolated 3,4-dihydro-3-keto-4,6,7-trimethyl-2-quinoxalinecarboxylic acid, III, which proved to be an important clue in the elucidation of the structure of riboflavin. We wish to report a total synthesis of this compound accomplished during a study of methods of preparing isoalloxazines.[3] The synthesis was carried out by condensation of 4,5-dimethyl-*o*-phenylenediamine with ethyl oxamalonate followed by methylation and saponification.

(1) Present address: General Electric Co., Plastic Division, Pittsfield, Massachusetts.

(2) Kuhn and Rudy, *Ber.*, **67**, 892; 1936 (1934); Kuhn, Reinemund and Weygand, *ibid.*, 1460 (1934).

(3) Tishler, Wellman and Ladenburg, THIS JOURNAL, **67**, 2165 (1945).