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

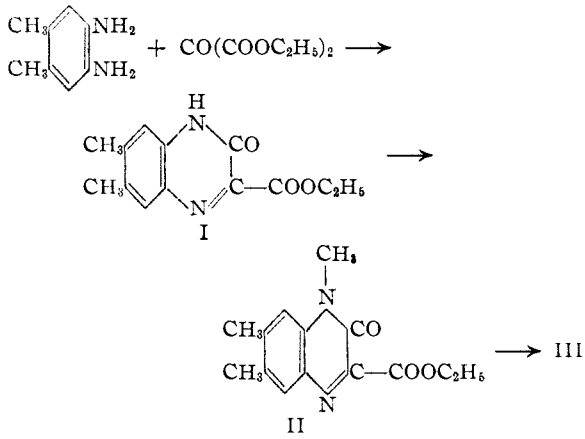
BY J. W. WELLMAN[1] AND MAX TISHLER

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).



The keto ester, II, was also prepared from ethyl oxomalonate and 1-methylamino-2-amino-4,5-dimethylbenzene. Because of the difficulty in preparing the latter[4] the first synthesis is preferable.

Experimental

3,4-Dihydro-3-keto-6,7-dimethyl-2-quinoxalinecarboxylic Acid, Ethyl Ester.—A solution of 6.5 g. of ethyl oxomalonate in 25 cc. of ethanol was added to a cooled solution of 5 g. of 4,5-dimethyl-*o*-phenylenediamine, and the mixture was refluxed for fifteen minutes. After storage at 5° for three hours, the product (8 g., 88% yield) was separated and recrystallized from ethanol. The product was obtained as matted needles; m. p. 199°.

Anal. Calcd. for $C_{13}H_{14}O_3N_2$: C, 63.41; H, 5.69. Found: C, 63.30; H, 5.81.

3,4-Dihydro-3-keto-4,6,7-trimethyl-2-quinoxalinecarboxylic Acid, Ethyl Ester.—Five grams of the above keto ester was added to a solution of sodium ethoxide in 25 cc. of ethanol prepared from 0.46 g. of sodium. The mixture was stirred fifteen minutes, 7 g. of methyl iodide was added and the mixture was refluxed. The reaction was completed in about fifteen minutes as evidenced by the disappearance of the insoluble sodio-derivative. The mixture was diluted with two volumes of ice water, and the precipitated product was recrystallized by dissolving in hot ethanol and adding water to slight turbidity; wt. 4.1 g., 94% yield, m. p. 125–126°.

Anal. Calcd. for $C_{14}H_{16}O_3N_2$: C, 64.62; H, 6.15. Found: C, 64.71; H, 6.40.

The same N-methyl keto ester was prepared by heating a mixture of 3.0 g. of 1-methylamino-2-amino-4,5-dimethylbenzene[4] and 4.0 g. of ethyl oxomalonate in 50 cc. of ethanol for one hour. After adding an equal volume of water, the product (wt. 4.5 g.) separated completely. After recrystallization from ethanol–water, the product melted at 124–126°.

3,4-Dihydro-3-keto-4,6,7-trimethyl-2-quinolxalinecarboxylic Acid.—To a solution of 0.5 g. of the above ester in 5 cc. of ethanol was added one equivalent of sodium ethoxide dissolved in 2 cc. of ethanol. One drop of water was added to the solution, whereupon a crystalline sodium salt separated within a few minutes. After chilling to 0° the product was separated, dissolved in ice water, and carefully acidified. The mixture was extracted with ether, and the ether extract, after drying with anhydrous magnesium sulfate, was concentrated to a small volume whereupon the acid crystallized. The product (0.25 g.) melted at 212–214° with carbon dioxide-liberation as previously recorded.[2] The identity of the acid was confirmed by decarboxylation to the known 3,4-dihydro-3-keto-4,6,7-trimethylquinoxaline; m. p. 174–175°.[2]

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RAHWAY, N. J.

RECEIVED OCTOBER 25, 1946

(4) Kuhn and Reinemund, *Ber.*, **67**, 1932 (1934).

Isolation of *l*-Arabinose

BY E. V. WHITE

Methods for the isolation of *l*-arabinose from natural sources have been described by several authors.[1] The procedure usually involves partial hydrolysis of a complex polysaccharide followed by fractional precipitation of portions more resistant to hydrolysis with alcohol and finally crystallization of the sugar from ethyl alcohol–water solution. The yield of arabinose is often low and the method is both tedious and expensive. A substantial improvement[2] is made when the hydrolyzate is dialyzed in an equal volume of distilled water. Residual polysaccharide and most hydrolytic decomposition products are thus separated from arabinose which collects in the dialyzate. Upon evaporation of the latter and addition of ethyl alcohol, *l*-arabinose crystallizes in good yield.

Procedure.—Two hundred grams of crude mesquite gum is dissolved in 1000 cc. of water, filtered to remove extraneous material and heated upon a boiling water-bath for thirty-six hours with 0.15 *N* sulfuric acid. The solution is then cooled, neutralized with barium carbonate, filtered and dialyzed against an equal volume of distilled water. The dialyzate is replaced by fresh water after twenty-four hours and the process repeated one or more times. The combined dialyzates are then evaporated under reduced pressure to a thin sirup and ethyl alcohol added slowly with stirring to 85% concentration. A small quantity of tarry material is separated in the centrifuge and the clear liquid re-evaporated to a sirup. The latter is thinned slightly with ethyl alcohol and *l*-arabinose crystallizes readily from the liquor. The over-all yield is about 75% of theoretical from three dialyzates.

(1) (a) Kiliani and Kohler, *Ber.*, **37**, 1210 (1904); (b) Tollens, *Hdb. biochem. Arbmeth.*, **2**, 64 (1909); (c) Anderson and Sands, "Organic Syntheses," **8**, 18 (1929); (d) Harding, *Sugar*, **24**, 656 (1922); *ibid.*, **25**, 124 (1923).

(2) White, THIS JOURNAL, **69**, 622 (1947).

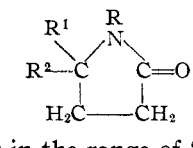
WOOD CONVERSION LABORATORY
UNIVERSITY OF IDAHO
MOSCOW, IDAHO

RECEIVED NOVEMBER 5, 1946

N-Substituted 2-Pyrrolidones

BY F. B. ZIENTY AND G. W. STEAHLY

Since γ-valerolactone now has become commercially available, it was of interest to prepare a number of N-substituted 2-pyrrolidones by thermal liquid phase reaction of lactones with amines



at temperatures in the range of 250° according to a procedure similar to one previously applied to γ-butyrolactone.[1]

Several of the compounds described, when

(1) (a) Späth and Lintner, *Ber.*, **69**, 2727 (1936); (b) catalytic vapor phase reaction of γ-butyrolactone with primary amines has been the subject of a patent; Schuster and Seib, U. S. Patent 2,267,757 (December 30, 1941); *C. A.*, **36**, 2566 (1942).