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
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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).

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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.

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(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).