

evaporated at 100°. The residue left behind was then triturated with water, filtered and the insoluble precipitate saved (see below). The aqueous filtrate was then saturated with hydrogen sulfide gas to precipitate tin as sulfide. After filtering off this tin sulfide precipitate and evaporating the filtrate to dryness no organic residue was recovered.

The insoluble precipitate (above) proved to be the desired reduction product. It was very insoluble in cold water, but separated from boiling water in colorless crystals melting at 142–143°. The total yield of pure crystallized hydantoin was 3.0 g. In a second experiment 8.8 g. of oenanthal-hydantoin was reduced under exactly the same conditions and yielded 8.8 g. of the desired reduced hydantoin.

Anal. Calcd. for $C_{10}H_{18}O_2N_2$: N, 14.14. Found: N, 14.17, 14.09.

Hydrolysis of the Reduced Hydantoin to α -Aminopelargonic Acid, $CH_3(CH_2)_6CH(NH_2)COOH$.—This hydantoin proved to be very resistant to hydrolysis by the action of barium hydroxide. Three grams of the pure reduced hydantoin was suspended in 1000 cc. of a hot, saturated solution of barium hydroxide and the mixture refluxed at its boiling point until the evolution of ammonia gas ceased. This actually required a digestion for fifty-six hours. The barium was then exactly precipitated as barium sulfate by adding the required amount of sulfuric acid, and bringing the solution to an exact neutral point to litmus. After filtering from barium sulfate, the clear aqueous solution was evaporated to dryness when we ob-

tained 2.4 g. of the required α -aminopelargonic acid or 92.3% of the theoretical.

This α -amino acid is very difficultly soluble in hot water, alcohol, benzene and glacial acetic acid. It was purified for analysis by dissolving in hot, dilute hydrochloric acid, and cooling, when the hydrochloride of the amino acid crystallized out as fine colorless needles. This salt showed no definite melting point but slowly underwent decomposition on heating. It was dried for analysis over phosphorus pentoxide in an Abderhalden vacuum drier.

Anal. Calcd. for $C_9H_{19}O_2NCl$: N, 6.68; Cl, 16.94. Found: N, 6.90, 6.52; Cl, 16.81.

In order to obtain the free α -aminopelargonic acid (I) 1 g. of the above hydrochloride was dissolved in hot water and the solution allowed to cool slowly. The amino acid separated in the form of colorless, flaky crystals. This acid did not show a definite melting point and underwent decomposition when heated between 236 and 256°, giving off dense vapors. The yield of free acid was 0.63 g. The crystals gave no test for chlorine, indicating complete dissociation of the hydrochloride in aqueous solution.

Anal. Calcd. for $C_9H_{19}O_2N$: C, 62.42; H, 10.98; N, 8.10. Found: C, 62.23; H, 10.83; N, 8.40, 7.90.

Summary

1. Oenanthal can be utilized with success for the synthesis of α -aminopelargonic acid by application of the aldehyde-hydantoin method of amino acid synthesis.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, KWANGSI UNIVERSITY]

Synthesis of 2-*n*-Butyl- α -naphthol

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In this short paper is described a method of synthesizing 2-*n*-butyl- α -naphthol, which promises to have practical value as an antiseptic. This compound is formed by reducing 2-*n*-butyryl- α -naphthol, which is in turn obtained by condensing α -naphthol with *n*-butyric acid in the presence of fused zinc chloride.

It has long been known that fatty acids react in a characteristic manner with phenols and resorcinol in the presence of fused zinc chloride giving hydroxy-ketones.² α -Naphthol also condenses with glacial acetic acid in the presence of acetic anhydride and zinc chloride giving 2-

acetyl- α -naphthol.³ The author finds that α -naphthol reacts likewise with *n*-butyric acid giving 2-*n*-butyryl- α -naphthol, m. p. 85–86°, which is identified by formation of its oxime and semicarbazone. A secondary product of the reaction is α -naphthol *n*-butyrate.

The hydroxy-ketones, such as 2-acetylhydroquinone, 4-acetylresorcinol, 4-propionylresorcinol, 2-propionylhydroquinone, 4-*n*-butyrylresorcinol, 4-acetylanisole, 4-acetylphenetole, 4-propionylphenetole, 2,5-dimethoxypropiofenone, 3,4-dimethoxypropiofenone, etc., which contain the hydroxyl or alkoxy group in the benzene ring, have been shown to undergo reduction to their corresponding alkyl derivatives by digesting with zinc amalgam and strong hydrochloric acid.⁴ In like manner 2-*n*-butyryl- α -naphthol is reduced

(3) Witt and Braun, *Ber.*, **47**, 3219 (1914).

(1) The author desires to express here his appreciation of the help given by Professor Treat B. Johnson of Yale University in organizing this paper for publication.

(2) Nencki and Sieber, *J. prakt. Chem.*, [2] **23**, 147, 537 (1887); Nencki and Schmid, *ibid.*, **23**, 546 (1887); Goldsweig and Kaiser, *ibid.*, [2] **43**, 86 (1891); Crepieux, *Bull. soc. chim.*, [3] **6**, 151 (1891); Nencki, *Ber.*, **26**, R587 (1893); Dzierzgowski, *ibid.*, **26**, R588 (1893); Pauly and Lockemann, *ibid.*, **48**, 30 (1915); Johnson and Lane, *THIS JOURNAL*, **43**, 348 (1921); Dohme, Cox and Miller, *ibid.*, **48**, 1688 (1926).

(4) Clemmensen, *ibid.*, **47**, 54 (1914); Johnson and Hodge, *THIS JOURNAL*, **35**, 1014 (1913); Johnson and Lane, *ibid.*, **43**, 348 (1921); Sonn, *Ber.*, **54**, 773 (1921).

to 2-*n*-butyl- α -naphthol according to the Clemmensen technique.

Experimental Part

2-*n*-Butyryl- α -naphthol.—Fifty-eight and four-tenths grams of α -naphthol was digested with 105.6 g. of *n*-butyric acid in the presence of 108 g. of fused zinc chloride for one minute. The mixture, while still warm, was then poured in a fine stream into 1200 cc. of cold water with stirring, whereupon the oil solidified to a brownish crystalline mass. After being filtered and dried, this reaction product was purified by fractionating in a vacuum. The following three fractions: (a) b. p. 135–150° at 3 mm., (b) b. p. 150–165° at 3 mm., and (c) b. p. 165–170° at 3 mm., were collected. Each fraction was redistilled at 1 mm. pressure, whence two main subfractions: (a) b. p. 125–130°, and (b) b. p. 145–152°, were finally obtained. The yield of the high boiling fraction (b. p. 145–152° at 1 mm.) was 34.3 g. It crystallized from hot petroleum ether in yellow rhombic crystals melting at 85–86°. The ketone also can be recrystallized from ether.

Anal. Calcd. for $C_{14}H_{14}O_2$: C, 78.46; H, 6.59. Found: C, 78.51, 78.39; H, 6.65, 6.73.

The low boiling fraction (b. p. 125–130° at 1 mm.) was proved to be α -naphthol *n*-butyrate. It was purified by recrystallization from a mixture of benzene and petroleum ether, separating in colorless needles, melting at 95.5–96.5°. The yield was 11.6 g. On treatment with hydroxylamine, it was changed into naphthol.

Anal. Calcd. for $C_{14}H_{14}O_2$: C, 78.46; H, 6.59. Found: C, 78.22, 78.35; H, 6.35, 6.50.

Oxime.—One and seven-hundredths grams of 2-*n*-butyryl- α -naphthol dissolved in a small volume of alcohol was treated with 0.7 g. of hydroxylamine hydrochloride and 0.53 g. of sodium carbonate dissolved in a small volume of water, and sufficient alcohol was added to obtain a uniform solution. This was then refluxed for four hours, and finally diluted with a large volume of water, whereupon the impure oxime precipitated. It was filtered, dried, and recrystallized from benzene and petroleum ether in the form of yellow needles, melting at 119° to a clear oil.

Anal. Calcd. for $C_{14}H_{14}O_2N$: N, 6.11. Found: N, 6.26, 6.33.

Semicarbazone.—One and seven-hundredths grams of 2-*n*-butyryl- α -naphthol dissolved in a small volume of alcohol was treated with 1.12 g. of semicarbazide hydrochloride and 0.53 g. of sodium carbonate dissolved in a small volume of water, and sufficient alcohol to obtain a uniform solution. This was heated on a water-bath for four hours, and water added to precipitate the semicarbazone. This was purified by dissolving in a mixture of alcohol, benzene and petroleum ether, and allowing to stand in a vacuum desiccator over sulfuric acid, whereupon the semicarbazone crystallized in microscopic crystals and melted at 201–202° to a clear oil. The yield was 0.3 g.

Anal. Calcd. for $C_{26}H_{17}O_3N_3$: N, 15.50. Found: N, 15.70, 15.61.

2-*n*-Butyryl- α -naphthol Methyl Ether.—Ten and seven-tenths grams of 2-*n*-butyryl- α -naphthol and 2.8 g. of potassium hydroxide were dissolved in 500 cc. of alcohol, and 5 cc. of dimethyl sulfate was added gradually drop by drop, while the solution was shaken vigorously. This was then heated at 50° for four hours to complete the reaction and the solution boiled for five minutes in order to destroy the excess of dimethyl sulfate and remove the excess of alcohol. This solution was then extracted with a large volume of benzene, the benzene solution dried with anhydrous sodium sulfate, filtered, and heated on a water-bath to remove the solvent. The oil left behind solidified on cooling and distilled at 155–157° at 1 mm. pressure. The yield was 6.5 g. After recrystallization from petroleum ether, it melted at 80–81°.

Anal. Calcd. for $C_{16}H_{16}O_2$: C, 78.90; H, 7.07. Found: C, 78.77, 78.83; H, 7.01, 6.94.

2-*n*-Butyryl- α -naphthol Ethyl Ether.—Ten and seven-tenths grams of 2-*n*-butyryl- α -naphthol dissolved in 500 cc. of alcohol was heated for eight hours with 6.5 g. of ethyl bromide and 2.8 g. of potassium hydroxide. After distilling off the alcohol the residue was extracted with a large volume of benzene; the solution was dried with anhydrous sodium sulfate, filtered, and finally heated on a water-bath to remove the solvent. The oil left behind solidified and distilled at 158–159° under 1 mm. pressure. After recrystallization from petroleum ether, it melted at 79–81°.

Anal. Calcd. for $C_{18}H_{18}O_2$: C, 79.29; H, 7.49. Found: C, 79.11; H, 7.57.

2-*n*-Butyl- α -naphthol.—Ten and seven-tenths grams of 2-*n*-butyryl- α -naphthol was digested with 50 g. of zinc amalgam suspended in a mixture of 50 cc. of concentrated hydrochloric acid and 50 cc. of water for seventeen hours. After each hour's boiling, 10 cc. of concentrated hydrochloric acid was added, until a total volume of 150 cc. of hydrochloric acid was used for the reaction. After the acid solution, with a layer of brown oil floating on the surface, was separated from the unreacted zinc amalgam and cooled, the crude 2-*n*-butyl- α -naphthol solidified. It was dried and distilled at 140–149° at 1 mm. pressure. The yield was 6.5 g. After purification by recrystallization from petroleum ether, it separated in colorless needles, melting at 73–74°. On keeping for two months it becomes colored.

Anal. Calcd. for $C_{14}H_{16}O$: C, 83.95; H, 8.06. Found: C, 83.99, 83.84; H, 8.24, 8.19.

Summary

1. α -Naphthol condenses normally with *n*-butyric acid giving 2-*n*-butyryl- α -naphthol.
2. 2-*n*-Butyl- α -naphthol is obtained by reduction of 2-*n*-butyryl- α -naphthol by Clemmensen's method.
3. The bactericidal properties of this new naphthol are under investigation.