
COMMUNICATION TO THE EDITOR

THE SYNTHESIS OF TWO STEREOISOMERIC 3,4-DIAMINO-2-TETRAHYDROFURAN-VALERIC ACIDS

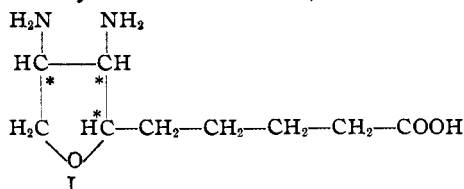
Sir:

Recently¹ a convenient procedure has been described for the preparation of 3,4-dicarboxy-2-furan-valeric acid. These studies have been continued in order to develop synthetic procedures for the preparation of biotin analogs. The purpose of the present communication is to report the synthesis of two stereoisomeric 3,4-diamino-2-tetrahydrofuran-valeric acids.

3,4-Dicarbethoxy-2-furanpentanol was prepared from 2-furanpentanol² (α -naphthyl-urethan m. p. 58–59°; calcd.: C, 74.27; H, 6.55; N, 4.33. Found: C, 73.97; H, 6.46; N, 4.41) and diethylacetylene dicarboxylate by the procedure outlined in the aforesaid publication. This material was subjected to high pressure hydrogenation and the reduction products were treated with hydrazine to yield two crystalline hydrazides, C₁₁H₂₂O₄N₄, m. p. 208–211° (calcd. C, 48.16; H, 8.08; N, 20.41. Found: C, 48.15; H, 7.85; N, 20.18) and m. p. 177–180° (Found: C, 48.01; H, 7.95; N, 20.27). These two dihydrazides of the stereoisomeric 3,4-dicarboxy-2-tetrahydrofuranpentanols were degraded by the Curtius method to the corresponding 3,4-diaminocarbethoxy-2-tetrahydrofuranpentanols, C₁₅H₂₈O₆N₂, m. p. 110–113° (calcd.: C, 54.21; H, 8.49; N, 8.42. Found: C, 53.92; H, 8.09; N, 8.57) and m. p. 128–130° (Found: C, 53.84; H, 8.19; N, 8.64). The primary alcohol group at the end of the aliphatic side chain was then converted to a carboxyl group by oxidation with chromic acid in

glacial acetic acid and the resulting 3,4-diaminocarbethoxy-2-tetrahydrofuran-valeric acids (m. p. 118–124° and 157–159°, respectively) were hydrolyzed with concentrated barium hydroxide to the corresponding 3,4-diamino-2-tetrahydrofuran-valeric acids. In order to characterize these compounds by means of sharply melting derivatives, the dibenzoyl methyl esters, m. p. 183–186° (calcd. C, 67.89; H, 6.64; N, 6.60. Found: C, 67.87; H, 6.38; N, 6.62) and m. p. 171–172° (Found: C, 67.62; H, 6.36; N, 6.68), respectively, were prepared, the higher melting isomer being derived from the higher melting hydrazide.

The molecule of 3,4-diamino-4-tetrahydrofuran-valeric acid I contains 3 asymmetric carbon atoms (denoted by means of asterisks).



and may exist in eight optically active forms. Four racemic mixtures therefore may be expected, two of which contain the amino groups in the *cis* and two which contain the amino groups in the *trans* configuration. The above-described diamino-carboxylic acids undoubtedly represent two of the four possible racemic forms; further work in this connection is at present under way in this Laboratory.

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(1) Hofmann, THIS JOURNAL, 66, 51 (1944).

(2) Hofmann, unpublished results.

NEW BOOKS

The Chemical Background for Engine Research. Editors, R. E. BURK, Director of Research, The Standard Oil Company, Cleveland, Ohio, and OLIVER GRUMMITT, Morley Chemistry Laboratory, Western Reserve University, Cleveland, Ohio. (Frontiers in Chemistry. Volume II.) Interscience Publishers, Inc., 215 Fourth Avenue, New York, N. Y., 1943. vii + 297 pp. Illustrated. 15.5 × 23.5 cm. Price, \$3.50.

"Prominent scientists report on recent investigations and interpretations of combustion processes and lubrication"—this brief advertisement which appears on the front jacket page of the volume expresses its contents much better than does the overly ambitious title. Actually, the work is a group of lectures on particular topics by six leading authorities; it is the second successful course of this type given by Western Reserve University in a commend-

able effort to present both the student and the mature chemist with an intelligible—but by no means superficial—view of current knowledge in the field.

Of the six chapters, "A Survey of Combustion Research," by Ernest F. Flock, presents a brief but excellent historical review and description of modern methods of studying flame travel. "Chemical Thermodynamics of Hydrocarbons," by Frederick D. Rossini, gives the calculation and best values of the entropy, heat and free energy of formation, and isomerization equilibria. "Synthetic Methods for Hydrocarbons," by Frank C. Whitmore, contains a survey of the typical laboratory Grignard reactions used, and a brief mention of some of the industrial methods of synthesis. "Kinetics of Flame and Combustion," by Guenther von Elbe, is restricted to the slow oxidation and self-ignition of hydrogen and the paraffin