ing clear prismatic crystals melted at 92–95° and, with a second, slightly less pure crop, amounted to 0.48 g. (24% calculated on the 2,3,4-triacetyl-β-D-arabinopyranosyl bromide).

Sodium Metaperiodate Oxidation of 1,5-Anhydro-D-arabitol.—The technique of Jackson and Hudson[13] was employed. The 1,5-anhydro-D-arabitol (0.1007 g.) was dissolved in a little water, treated with 5.0 ml. of 0.480 *M* sodium metaperiodate solution and the solution diluted to 25.0 ml. with water. After twenty-three hours at room temperature a 5-ml. sample was titrated for formic acid and for residual oxidant. On a basis of one mole of 1,5-anhydro-D-arabitol, the reaction consumed 1.95 moles of sodium metaperiodate and produced 1.03 moles of formic acid, in a manner similar to the behavior of 1,5-anhydro-xylitol (ref. 1e).

2,3,4-Triacetyl-1,5-anhydro-D-arabitol.—One-half gram of 1,5-anhydro-D-arabitol was dissolved in 2 ml. of pyridine and treated with 1.37 ml. of acetic anhydride. After warming the solution in a 110° oven for twenty minutes it was cooled and diluted with 10 ml. of chloroform. The solution was then washed twice with ice-cold 3 *N* sulfuric acid, once with aqueous sodium bicarbonate and finally dried over calcium chloride. It was then freed of desiccant by filtration and concentrated on a steam-bath to a sirup. Dissolved in 1 ml. of ethanol, the material crystallized spontaneously on scratching. The minute clusters of needle-shaped crystals were washed with ethanol; a second crop of equally pure material was obtained from the filtrate by the addition of pentane to make a total of 0.574 g. (59%). Recrystallized once from a mixture of two parts of absolute alcohol and four parts of benzene the triacetate melted at 58°; further recrystallization failed to change this value. In chloroform the 1,5-anhydro-D-arabitol triacetate rotated −74.2° (*c*, 1.018).

Anal. Calcd. for $C_{11}H_{16}O_7$: C, 50.77; H, 6.19. Found: C, 50.47; H, 6.18.

2,3,4-Tribenzoyl-1,5-anhydro-D-arabitol.—1,5-Anhydro-D-arabitol (0.3004 g.) was dissolved in pyridine (2.0 ml.) and treated with benzoyl chloride (1 ml.). After one-half hour at 40° the reaction mixture was diluted with cold aqueous sodium bicarbonate solution and the crystalline precipitate removed by filtration; yield quantitative. Twice recrystallized from six parts of ethanol, the product melted at 120–121° and exhibited in chloroform the high negative rotation of −220°.

Anal. Calcd. for $C_{26}H_{22}O_7$: C, 69.95; H, 4.97. Found: C, 70.17; H, 4.96.

Summary

1,5-Anhydro-D-arabitol has been prepared through the reductive desulfurization with Raney nickel of crystalline 2′-naphthyl 1-thio-α-D-arabinopyranoside triacetate, sirupy phenyl 1-thio-D-arabinopyranoside triacetate and sirupy ethyl triacetyl-D-arabinopyranosyl xanthate. Its analysis and those of its derivatives, as well as its behavior with sodium metaperiodate, serve to confirm its structure. Its configuration is confirmed by the fact that it is optically active.

BETHESDA, MARYLAND RECEIVED MARCH 6, 1947

(13) E. L. Jackson and C. S. Hudson, THIS JOURNAL, **59**, 994 (1937).

[CONTRIBUTION FROM THE DEPARTMENT OF AGRICULTURAL CHEMISTRY, NORTH DAKOTA AGRICULTURAL COLLEGE AND EXPERIMENT STATION]

A New Synthesis of *dl*-Aspartic Acid[1]

BY HAROLD J. KLOSTERMAN AND EDGAR PAGE PAINTER[2]

Aspartic acid has been synthesized by the addition of ammonia to fumaric acid[3,4] or to diethyl fumarate[5]; by the reduction of diethyl oximino succinate,[6,7] and by the benzamidomalonic ester method.[8] While the first two methods gave fairly good yields in the single steps described, the addition of ammonia required pressure equipment and diethyloximinosuccinate was not prepared in good yield. The yields by the benzamidomalonic ester synthesis were poor when calculated on the original malonic ester.

Since γ-butyrolactone is now readily available and can be converted to α-amino-γ-hydroxybutyric acid in satisfactory yields[9] it seemed that the latter compound might be readily converted to aspartic acid by oxidation of the carbinol.

Oxidation of α-amino-γ-hydroxybutyric acid failed to yield aspartic acid. However, oxidation of the benzamido derivative by the method of Billman and Parker[10] gave satisfactory yields of benzamido-aspartic acid. This compound was hydrolyzed to aspartic acid in good yields. The over-all yields of aspartic acid were approximately 40%.

During the benzoylation of α-amino-γ-hydroxybutyric acid a small amount of the γ-benzoic acid ester of α-benzamido-γ-hydroxybutyric acid was obtained.

Experimental

α-Bromo-γ-butyrolactone.—The method of Livak, *et al.*,[9] was used to prepare 1620 g. of α-bromo-γ-butyrolactone [b. p. 137 to 140° at 20 mm.] from 908 g. of γ-butyrolactone. The yield of crude product was 93%.

α-Amino-γ-hydroxybutyric Acid.—The α-bromo-γ-butyrolactone (1540 g.) was treated with ammonium hydroxide[9] to give 493 g. of α-amino-γ-hydroxybutyric acid, m. p. 180° (uncor.).

Anal. Calcd. for $C_4H_9NO_3$: N, 11.76. Found: N, 11.70.

An additional 401 g. of α-amino-γ-butyrolactone hydrobromide, m. p. 212°, were recovered from the filtrates.[9] The total yield of amino acid was about 68%.

(1) Published by permission of the Director of the North Dakota Agricultural Experimental Station.

(2) Present address: Division of Chemistry, College of Agriculture, University of California, Davis.

(3) Tutiya, Yosio., *J. Agr. Chem. Soc., Japan*, **17**, 706 (1941).

(4) Enkrist and Laasonen, *Ber.*, **72B**, 1927 (1939).

(5) Dunn and Fox, *J. Biol. Chem.*, **101**, 493 (1933).

(6) Hamlin and Hartung, *ibid.*, **145**, 349 (1942).

(7) Cocker, *J. Chem. Soc.*, 1489 (1940).

(8) Redemann and Dunn, *J. Biol. Chem.*, **130**, 341 (1939).

(9) Livak, Britton, VanderWeele and Murray, THIS JOURNAL, **67**, 2218 (1945).

(10) Billman and Parker, *ibid.*, **66**, 538 (1944); **65**, 2455 (1943).

Anal. Calcd. for $C_4H_8NO_2Br$: N, 7.70. Found: N, 7.68.

α-Benzamido-γ-hydroxybutyric Acid.—In a typical run 59.5 g. (0.5 mole) of α-amino-γ-hydroxybutyric acid was dissolved in 500 ml. of *M* sodium hydroxide. The solution was cooled in an ice-bath and 58 ml. of benzoyl chloride and 250 ml. of 2 *M* sodium hydroxide were added simultaneously at such a rate that the temperature remained below 10° and the solution alkaline. The addition required about one hour. After stirring for two hours more, the solution was acidified with 60 ml. of concentrated hydrochloric acid and thoroughly extracted with ether to remove benzoic acid and the small amount of α-benzamido-γ-benzoxybutyric acid which forms. The aqueous solution upon cooling overnight in the refrigerator yielded 95 g. of α-benzamido-γ-hydroxybutyric acid which melted at 126–127°. This product contained 5.92% N. Recrystallization by dissolving in sodium hydroxide and addition of acid raised the nitrogen content but the melting point remained unchanged.

Anal. Calcd. for $C_{11}H_{13}NO_4$: N, 6.28. Found: N, 6.18%.

Similar yields were obtained by benzoylating the lactone hydrobromide, provided the calculated amount of 2 *M* sodium hydroxide to neutralize the hydrobromide was added in addition to that used for benzoylation.

α-Benzamido-γ-benzoxybutyric Acid.—The ether extracts from the previous reaction were combined and evaporated nearly to dryness on the steam-bath. The crystalline mass was filtered off and washed with a little ether to remove any benzoic acid. The product (3 g.) was dissolved in the minimum amount of hot 95% ethanol and crystallized by addition of an equal volume of water and cooling the solution. The compound crystallizes as thin plates melting at 198°. These crystals were dissolved in dilute sodium hydroxide, heated for fifteen minutes, then the solution was cooled and acidified. Benzoic acid separated out and was extracted with ether. The aqueous layer was cooled in the refrigerator overnight and crystals melting at 125° separated. A mixed melting point with a known sample of α-benzamido-γ-hydroxybutyric acid melted at 125–126°.

Anal. Calcd. for $C_{18}H_{17}NO_6$: N, 4.28. Found: N, 4.27.

***dl*-Benzamido-aspartic Acid.**—Forty grams of crude α-benzamido-γ-hydroxybutyric acid was dissolved in 300 ml. of water containing 10 g. of sodium hydroxide. The solution was cooled in an ice-bath and 40 g. of potassium permanganate added at such a rate that the temperature never exceeded 10°. When all the permanganate dissolved, the solution was allowed to reach room temperature and the manganese dioxide filtered off. After the excess permanganate was reduced with methanol, decolorizing carbon was added and the suspension filtered. The filtrate was acidified with excess hydrochloric acid and allowed to set in the refrigerator overnight. The crystalline product of *dl*-benzamido-aspartic acid weighed 34 g. This is the monohydrate as reported by Karrer and Schneider[11] and by Cocker[7] and does not give a sharp melting point.

Anal. Calcd. for $C_{11}H_{11}NO_5.H_2O$: N, 5.48. Found: N, 5.36.

A sample which was dried in a vacuum for four hours at 110° melted at 176–177° (reported[11] 175°).

Anal. Calcd. for $C_{11}H_{11}NO_5$: N, 5.90. Found: N, 5.87.

***dl*-Aspartic Acid.**—Twenty-six grams of benzamido-aspartic acid monohydrate were refluxed for six hours in 200 ml. of water containing 15 ml. of 12 *M* hydrochloric acid. The benzoic acid which crystallized upon cooling was filtered off and the rest extracted from the filtrate with ether. The solution was evaporated to dryness (vacuum pump) and the residue was dissolved in 150 ml. of 95% ethanol. Crystallization took place immediately upon the addition of 15 ml. of pyridine. After setting overnight in the refrigerator the product was filtered out, washed with cold water, alcohol and ether. The recovery of aspartic acid from the benzamido derivative was 95%. The product decomposed above 280°.

Anal. Calcd. for $C_4H_7NO_4$: N, 10.53. Found: N, 10.42.

Acknowledgment.—The γ-butyrolactone was generously supplied by the Cliffs Dow Chemical Company.

Summary

A convenient synthesis of *dl*-aspartic acid is described. α-Amino-γ-hydroxybutyric acid (or the lactone hydrobromide) prepared from γ-butyrolactone was benzoylated to give α-benzamido-γ-hydroxybutyric acid. This compound was oxidized by alkaline potassium permanganate to benzamido-aspartic acid, from which *dl*-aspartic acid was obtained by hydrolysis.

(11) Karrer and Schneider, *Helv. Chim. Acta*, **13**, 1286 (1930).

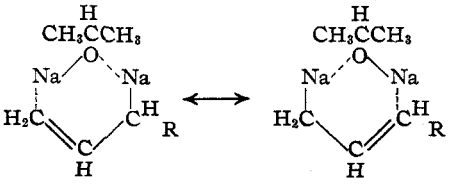
FARGO, NORTH DAKOTA RECEIVED JANUARY 25, 1947

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Polymerization. VII. The Structure of the Alfin Catalyst[1]

BY AVERY A. MORTON AND MURIEL E. T. HOLDEN[1a]

In the previous paper[2] the combination of sodium isopropoxide with the metalation product of propylene or certain other olefins was shown to have the unique property of inducing the catalytic polymerization of dienes. This behavior is distinct from that shown by alkenylsodium compounds alone, which merely add to dienes to form a series of adducts. The combination was called an Alfin catalyst. As a structure for the complex, the cyclic doubly coördinated formula shown below in two forms was suggested. One criterion of such a structure is that the alkenyl-sodium compound could exist in two possible forms that would be regarded as allylic isomers or as structures that might contribute to resonance. A second cri-



(1) This study was carried out under the auspices of the Rubber Reserve Company.

(1a) Present address: E. I. du Pont de Nemours Company, Photo Products Department, Parlin, New Jersey.

(2) Morton, Magat and Letsinger, THIS JOURNAL, **69**, 950 (1947).