dissolved in water, the solution filtered and the filtrate again distilled to dryness. This operation was repeated several times in order to remove the benzoic and crotonic acids. The final residue was 10 g. of crystalline mass, which gave 4.7 g. of crystals (m. p. 88.5°) from a mixture of ether and carbon tetrachloride, or 20% of the theoretical. A mixed m. p. with 2-methylglycidic acid (m. p. 88.5°) obtained from crotonic acid with hypochlorous acid gave 88.5°.

Anal. Subs., 0.008885: H_2O, 0.00479; CO_2: 0.01542. Calcd. for $C_4H_6O_3$: H, 5.93; C, 47.04. Found: H, 6.03; C, 47.33.

Summary

1. An improved method of oxidation of crotonic acid with hypochlorous acid is reported. The 1-chloro-2-hydroxybutyric acid (m. p. 62–63°) is obtained in 30% yield, its potassium salt in 80% yield; the 2-methylglycidic acid (m. p. 88.5°) in 64%, and its potassium salt in 86% yield. The hydrolysis of the crude 2-methylglycidic acid gives the *dl*-erythro-1,2-dihydroxybutyric acid (m. p. 81.5°) in 60% yield at 100° and in 71% yield at room temperature.

2. It is shown that the 2-methylglycidic acid (m. p. 88.5°) hydrolyzes in dilute aqueous solution quantitatively to *dl*-erythro-1,2-dihydroxybutyric acid (m. p. 81.5°).

3. The oxidation of crotonic acid with perbenzoic acid in non-aqueous solution is reported. The oxidation yields the same 2-methylglycidic acid (m. p. 88.5°) that is obtained from the crotonic acid with hypochlorous acid.

Chicago, Illinois

[Contribution from the Kent Chemical Laboratory, University of Chicago]

OXIDATION OF UNSATURATED COMPOUNDS. V. STUDIES IN THE OXIDATION OF CONJUGATED SYSTEMS. OXIDATION OF PENTENOIC AND HEXENOIC ACIDS

By Géza Braun[1]

Received November 27, 1929 Published August 5, 1930

All the previous publications in this series were made preliminary to a systematic study of oxidation of conjugated systems. The investigation of vinylacrylic and sorbic acids was begun years ago. It was found that the vinylacrylic acid is easily oxidizable with hypochlorous acid but suffers partial decomposition in the oxidation with chlorates and perbenzoic acid. In contrast to this, sorbic acid is smoothly oxidizable with all these agents with good yield. The oxidation of sorbic acid with perbenzoic acid especially offers interesting results because it takes up the first molecule of peracid much more easily than the second, so there seems to be a possibility of a successful study of the mechanism of the oxidation.

But before this can be made it is necessary to study all the theoretically

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[1] International Research Fellow in organic chemistry from Hungary, 1926–1928.

possible valeric and caproic acids as well as the corresponding derivatives of the glycidic acid. With this idea in mind the preparation of all the theoretically possible *dl*-1,2-dihydroxyvaleric and caproic acids was accomplished by the oxidation of α,β-pentenoic and α,β-hexenoic acids. The oxidations were carried out in the same manner that was reported in the case of crotonic and isocrotonic acids.[2]

The α,β-pentenoic acid (m. p. 9.5–10°) gave by oxidation with silver chlorate the *dl*-1,2-dihydroxyvaleric acid (m. p. 75°) with 80% yield, whereas with perbenzoic acid it yielded the *dl*-1,2-dihydroxyvaleric acid (m. p. 106°) with 75% yield.

The α,β-hexenoic acid (m. p. 33–34°) gave with silver chlorate the *dl*-1,2-dihydroxycaproic acid (m. p. 108.5°) with 86% yield and with perbenzoic acid the *dl*-1,2-dihydroxycaproic acid (m. p. 99.5°) with 46% yield.

Proof of the configuration of these acids is in progress.

Experimental Part

Materials.—The α,β-pentenoic acid (m. p. 9.5°) and the α,β-hexenoic acid (m. p. 34°) were prepared according to Doebner's method.[3]

Oxidation of α,β-Pentenoic Acid (m. p. 9.5°)

1. **With Silver Chlorate.**—Ten grams of pentenoic acid was dissolved in 500 cc. of water which contained 0.05 g. of osmic acid and 7.6 g. of silver chlorate was gradually added while the solution was kept in an ice-bath as described in the case of crotonic acid under III (B). The crude reaction product was 13.2 g. of a crystalline mass, which gave in two crops 10.7 g. of crystals (m. p. 75°) from ethyl acetate or 80% of the theoretical. The m. p. of the product could not be changed by further crystallization.

Titration. Subs., 0.3824: 28.67 cc. of 0.1 *N* alkali. Calcd. mol. wt. for $C_5H_{10}O_4$: 134.08. Found: 133.4.

Anal. Subs., 0.00898: H_2O, 0.00613; CO_2, 0.01488. Calcd. for $C_5H_{10}O_4$: H, 7.52; C, 44.79. Found: H, 7.64; C, 45.19.

The acid has almost identical properties with the *dl*-threo-1,2-dihydroxybutyric acid, m. p. 74–75°.

Phenylhydrazide.—One gram of acid gave 1.4 g. of phenylhydrazide (m. p. 140.5°) from absolute alcohol. The salt is insoluble in cold absolute alcohol.

Anal. Subs., 0.00546: 0.551 cc. of N_2 (22°, 750 mm.). Calcd. for $C_{11}H_{16}O_3N_2 \cdot H_2O$: N, 11.57. Found: 11.52.

The substance partially loses its water of crystallization over phosphorus pentoxide *in vacuo*.

2. **With Perbenzoic Acid.**—Ten grams of pentenoic acid was dissolved in 500 cc. of water and oxidized with 25 g. of perbenzoic acid in 125 cc. of chloroform under continuous shaking at 10° in the usual manner. The yield was 12.5 g. of sirup which gave 10.2 g. of crystals (m. p. 105–106°) from ethyl acetate or 75% of the theoretical. The recrystallized product melts at 106°.

Titration. Subs., 0.4114: 31.09 cc. of 0.1 *N* of alkali. Calcd. mol. wt. for $C_5H_{10}O_4$: 134.08. Found: 132.3.

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[2] Géza Braun, THIS JOURNAL, **51**, 228 (1929).

[3] Auwers, *Ann.*, **432**, 46 (1923); Goldberg, *J. Chem. Soc.*, 2343 (1928).

Anal. Subs., 0.009023: H_2O, 0.00616; CO_2, 0.01496. Calcd. for $C_5H_{10}O_4$: H, 7.52; C, 44.79. Found: H, 7.64; C, 45.21.

The acid has almost the same properties as the *dl*-erythro-1,2-dihydroxybutyric acid (m. p. 81.5°).

Phenylhydrazide.—One gram of acid gave 0.75 g. of recrystallized phenylhydrazide (m. p. 119–119.5°) from absolute alcohol. The salt is moderately soluble in cold absolute alcohol.

Anal. Subs., 0.00431: N, 0.471 cc. (21.5°, 754 mm.). Calcd. for $C_{11}H_{16}O_3N_2$: N, 12.49. Found: N, 12.54.

Oxidation of α,β-Hexenoic Acid (m. p. 34°)

1. **With Silver Chlorate.**—Twenty grams of acid was suspended (partially dissolved) in one liter of water and oxidized by gradual addition of 13.6 g. of silver chlorate in the presence of 0.1 g. of osmic acid at 0° in the usual manner. The yield was 25.2 g. of a crystalline mass which gave 22.6 g. of crystals (m. p. 108°) from ethyl acetate, or 86% of the theoretical. The residue from ethyl acetate crystallized again. The recrystallized product melted at 108.5°.

Titration. Subs., 0.4354: 29.67 cc. of 0.1 *N* alkali. Calcd. mol. wt. for $C_6H_{12}O_4$: 148.1. Found: 146.7.

Anal. Subs., 0.009572: H_2O, 0.00693; CO_2, 0.0172. Calcd. for $C_6H_{12}O_4$: H, 8.17; C, 48.61. Found: H, 8.1; C, 49.00.

The acid was found to be very soluble in hot water and hot ethyl acetate, moderately soluble in cold water and ether, insoluble in chloroform.

Phenylhydrazide.—One gram of acid gave 1.5 g. of phenylhydrazide (m. p. 141.5–142°) from absolute alcohol. The salt is insoluble in cold absolute alcohol.

Anal. Subs., 0.00471: 0.450 cc. of N_2 (20.5°, 740 mm.). Calcd. for $C_{12}H_{18}O_3N_2 \cdot H_2O$: N, 10.93. Found: N, 10.82.

2. **Perbenzoic Acid.**—Ten grams of acid was dissolved in 125 cc. of chloroform which contained 25 g. of peracid and after addition of 500 cc. of water the mixture was shaken at 10°, etc., as usual. The yield was 8.9 g. of a yellowish sirup which gave 6.0 g. of crystals (m. p. 98.5°) from ethyl acetate or 46% of the theoretical. The recrystallized product melted at 99.5°.

Titration. Subs., 0.3666: 24.95 cc. of 0.1 *N* alkali. Calcd. mol. wt. for $C_6H_{12}O_4$: 148.1. Found: 147.0.

Anal. Subs., 0.00884: H_2O, 0.00638; CO_2, 0.01586. Calcd. for $C_6H_{12}O_4$: H, 8.17; C, 48.61. Found: H, 8.08; C, 48.93.

The acid is very soluble in water, hot ethyl acetate and alcohol, moderately soluble in cold ethyl acetate or in ether, insoluble in chloroform.

Phenylhydrazide.—One gram of acid gave 0.75 g. of recrystallized phenylhydrazide (m. p. 120–121°) from absolute alcohol. The compound is moderately soluble in cold absolute alcohol.

Anal. Subs., 0.004367: N_2, 0.454 cc. (24°, 752 mm.). Calcd. for $C_{12}H_{18}O_3N_2$: N_2, 11.76. Found: N_2, 11.82.

Summary

The preparation of all the theoretically possible *dl*-1,2-dihydroxyvaleric and caproic acids is reported. The α,β-pentenoic acid (m. p. 9.5°) gives by oxidation with silver chlorate the *dl*-1,2-dihydroxyvaleric acid (m. p. 75°) with 80% yield and with perbenzoic acid the *dl*-1,2-dihydroxyvaleric acid (m. p. 106°) with 75% yield.

The α,β-hexenoic acid (m. p. 33–34°) gives with silver chlorate the *dl*-1,2-dihydroxycaproic acid (m. p. 108.5°) with 86% yield and with perbenzoic acid the *dl*-1,2-dihydroxycaproic acid (m. p. 99.5°) with 46% yield.

CHICAGO, ILLINOIS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE]

STRUCTURE OF THE CHLORALOSES. BETA-XYLOCHLORALOSE

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RECEIVED NOVEMBER 27, 1929 PUBLISHED AUGUST 5, 1930

In a preceding paper[1] it has been shown that the available evidence indicates an acetal type of linkage for the union of chloral with glucose in β-glucochloralose rather than the carbon–carbon linkage depicted by the older formulas in the literature. The attempt to determine the configuration of the β-glucochloralose by means of methylation failed due to the resistance to hydrolysis of the partially dechlorinated trimethyl-β-glucochloralose.

In the literature[2] it has been shown that β-xylochloralose (formula III) yields chloralic acid (Formula II), which is identical with the acid obtained by oxidation of β-glucochloralose (Formula I), the formulas being used with the limitations of the preceding report.[1] The β-xylochloralose was accordingly drawn into these investigations in the hope that its greater range of solubility would make it possible completely to remove the chlorine, or on failure of this to hydrolyze the partially dechlorinated compound. Other than the chloralic acid,[2] the only definite derivative of β-xylochloralose reported in the literature is the dibenzoate.[3]

The β-xylochloralose was prepared according to the method of Hanriot. By further treatment with chloral hydrate and sulfuric acid, β-xylochloralose was converted to a crystalline dichloralxylose which could not be acetylated. This would indicate the absence of a free hydroxyl group in the dichloralxylose and could only be interpreted in terms of the acetal type of linkage as was the case with the conversion of β-glucochloralose to the dichloralglucoses. The possible structures for the dichloralxylose would accordingly be analogous to the corresponding acetone derivatives reported by Freudenberg and Svanberg.[4] Experimental evidence indicates the existence of at least two isomeric dichloralxyloses.

Dimethyl β-xylochloralose was obtained by methylation of β-xylochloralose with dimethyl sulfate. Repeated methylations failed to increase the methoxy content above that for the di- derivative. Attempts to

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[1] Coles, Goodhue and Hixon, THIS JOURNAL, **51**, 519 (1929).

[2] Hanriot, *Compt. rend.*, **120**, 153 (1895); **148**, 487 (1909); *Bull. soc. chim.*, [4] **5**, 819 (1909); *Ann. chim. phys.*, [8] **18**, 466 (1909).

[3] Hanriot, *ibid.*, [8] **18**, 466 (1909).

[4] Freudenberg and Svanberg, *Ber.*, **55**, 3239 (1922).