droxylated product is proved by conversion of the compound into the racemic tartaric acid in acid solution.

2. The treatment of the *dl*-threo-1,2-dihydroxy-3-chlorobutyric acid with silver oxide gives the *dl*-threonic acid in 46% yield. It is shown that in this reaction no inversion occurs.

3. The preparation and properties of *dl*-threonic acid (m. p. 98°) are reported. The *dl*-threonic acid is a free acid and does not form a lactone under the conditions in which the *dl*-erythronic acid can be isolated only as a lactone.

4. The proof of configuration of the *dl*-1,2-dihydroxybutyric acids is reported. The proof is based on the fact that the *dl*-threo-1,2-dihydroxy-3-chlorobutyric acid may be converted into racemic acid, and on the other hand it may be reduced to the *dl*-1,2-dihydroxybutyric acid, m. p. 74–75°, with a yield of 70%. This shows clearly that the *dl*-1,2-dihydroxybutyric acid, m. p. 74°, has the same configuration as racemic acid and the other possible acid—the *dl*-1,2-dihydroxybutyric acid m. p. 81.5°—has a configuration corresponding to mesotartaric acid.

The assignment of the prefixes "threo" and "erythro" which were previously suggested for the *dl*-1,2-dihydroxybutyric acids of melting points 74.5 and 81.5° respectively, is therefore justified.

CHICAGO, ILLINOIS

[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY, UNIVERSITY OF CHICAGO]

OXIDATION OF UNSATURATED COMPOUNDS. IV. OXIDATION OF CROTONIC ACID WITH HYPOCHLOROUS AND PERBENZOIC ACIDS

BY GÉZA BRAUN[1]

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The oxidation of crotonic acid with hypochlorous acid was first reported by Melikoff.[2] After the configuration of the *dl*-1,2-dihydroxybutyric acids had been established,[3] it was important to investigate Melikoff's work quantitatively. The oxidation of crotonic acid with hypochlorous acid to the *dl*-erythro-1,2-dihydroxybutyric acid (m. p. 81.5°) involves three operations: (a) addition of hypochlorous acid to crotonic acid, which yields the 1-chloro-2-hydroxybutyric acid; (b) treatment of 1-chloro-2-hydroxybutyric acid with alkali in order to obtain the 2-methylglycidic acid; (c) hydrolysis of 2-methylglycidic acid to the *dl*-1,2-dihydroxybutyric acid.

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

[2] Melikoff, *Ann.*, **234**, 197 (1886); see also Glattfeld and Woodruff, THIS JOURNAL, **49**, 2309 (1927).

[3] Géza Braun, *ibid.*, **52**, 3176 (1930).

In the first operation (a) it was found that the reaction between the crotonic and hypochlorous acids may be indicated by the equation

$$CH_3CH{=}CHCOOH + Cl_2 + H_2O \longrightarrow CH_3CHOHCHClCOOH + HCl$$

The pure potassium salt of 1-chloro-2-hydroxybutyric acid was obtained from alcohol with 80% yield and the free acid, without isolation of a pure salt, with 30% yield.

The preparation of 2-methylglycidic acid (b) has been greatly improved and simplified. The pure acid (m. p. 88.5°) was obtained from the crude reaction mixture in 64% yield.

The *dl*-erythro-1,2-dihydroxybutyric acid (m. p. 81.5°) (c) was obtained from the crotonic acid, without the isolation of the intermediate products, in 70–72% yield. The pure 2-methylglycidic acid (m. p. 88.5°) hydrolyzes quantitatively to the above acid.

In order to obtain comparative results, the crotonic acid was oxidized with perbenzoic acid in non-aqueous solution. The result was the 2-methylglycidic acid (m. p. 88.5°) with about 20% yield. It was found therefore that the perbenzoic acid yields the same ethylene oxide compound that is obtained in the oxidation with hypochlorous acid.

The oxidation of pure isocrotonic acid with hypochlorous acid and the proof of configuration of the intermediate compounds is in progress.

Experimental Part

1. **1-Chloro-2-hydroxybutyric Acid.**—Twenty grams of crotonic acid was dissolved in one liter of water which contained 500 g. of chopped ice. Then, under effective stirring and ice cooling, a slow stream of chlorine was conducted into the solution until absorption was complete (about three hours). The slight excess of chlorine was removed at reduced pressure in the cold.

(a) **Potassium Salt of the Acid.**—The solution was neutralized with 43 g. of potassium bicarbonate at 0° and the water removed at reduced pressure. The crystalline residue was washed with cold absolute alcohol and then treated with 150 cc. of hot alcohol. The filtrate from the potassium chloride deposited 15.5 g. of crystals after cooling; after addition of an equal volume of ether a further crystallization occurred (20.5 g.) making a total yield 36.0 g. of potassium salt or 80% of the theoretical. The salt contained only a trace of potassium chloride.

Anal. Subs., 0.4952: 25.28 cc. of 0.1 *N* $AgNO_3$. Calcd. for $C_4H_6O_3KCl{\cdot}H_2O$: Cl, 18.22. Found: Cl, 18.13.

(b) **Free Acid.**—Another chlorinated solution of 20 g. of crotonic acid was neutralized with 43 g. of potassium bicarbonate and the solution concentrated at reduced pressure to small volume. After the neutral solution had been extracted with ether, the theoretical amount of dilute hydrochloric acid was added to the solution and the chlorohydroxybutyric acid thus freed extracted with ether, etc., as usual. The residue of the united ethereal solutions was 33.0 g. of a pale yellow sirup, which was dissolved in 10 cc. of ethyl acetate–carbon tetrachloride mixture, cooled to 0° and seeded. After ten hours' standing on ice the solution yielded 9.5 g. of crystals (m. p. 62–63°), or 30% of the theoretical (Melikoff's acid melted at 62–63°). The seeding crystals were obtained by letting the sirupy acid stand for several weeks in a desiccator.

2. **2-Methylglycidic Acid.** (a) **Potassium Salt.**—To a chlorinated solution of

20 g. of crotonic acid an ice cold dilute solution of 45 g. of potassium hydroxide was added under stirring in the presence of much ice. The solution was then allowed to stand overnight at 0° and afterward for three to four hours at room temperature. The slight excess of potassium hydroxide was neutralized with hydrochloric acid, the solution distilled to dryness at reduced pressure, the residue dehydrated with absolute alcohol and treated with 100 cc. of hot absolute alcohol. To the filtrate from the potassium chloride 100 cc. of absolute ether was added, whereupon the potassium methylglycidate crystallized immediately (25.5 g.). From the mother liquor a second crop of 2.6 g. of crystals was obtained, making a total yield of 28.1 g. of crystals (dried over phosphorus pentoxide *in vacuo* to constant weight) or 86% of the theoretical. The crystals are very soluble in hot absolute alcohol and are very hygroscopic.

(b) **Free Acid.**—To the concentrated aqueous solution of potassium methylglycidate—prepared from three times 20 g. of crotonic acid as described above—the theoretical amount of dilute hydrochloric acid was added and the solution extracted several times with ether. The aqueous solution was further concentrated at reduced pressure and the solution was again extracted with ether. The residue of the united ethereal solutions weighed 69 g. and was a pale yellow sirup which crystallized immediately. This was dissolved in 15 cc. of warm ether and then 45 cc. of warm carbon tetrachloride was added and the solution was put on ice. The yield was 46 g. of crystals (m. p. 86°), or 64% of the theoretical. The crystals were dissolved in 45 cc. of hot carbon tetrachloride and 20 cc. of warm ether was added. The solution deposited in the course of several hours at room temperature 40 g. of crystals (m. p. 88.5°).

Titration. Subs., 0.3620: 34.34 cc. of 0.1 N alkali. Calcd. mol. wt. for $C_4H_6O_3$: 102.05. Found: 105.4.

Hydrolysis of 2-Methylglycidic Acid.—Four grams of acid (m. p. 88.5°) was dissolved in 200 cc. of water and allowed to stand for six weeks at room temperature. Then the water was removed at room temperature and the residue dried for several hours at 40°. The hard, crystalline residue weighed 4.6 g. or 97% of the theoretical; this gave 4.0 g. of crystals (m. p. 81.5–82°) from ethyl acetate; mixed m. p. with *dl*-erythro-1,2-dihydroxybutyric acid (m. p. 81.5°) obtained from crotonic acid with perbenzoic acid, 81.5°.

3. ***dl*-Erythro-1,2-dihydroxybutyric Acid.**—(a) A chlorinated solution of 20 g. of crotonic acid was treated with 45 g. of potassium hydroxide below 0° as is described under 2(a). The excess of potassium hydroxide was neutralized and then 80 g. of 10% hydrochloric acid was added and the solution kept at 98° for six hours in a water-bath. The water was removed at reduced pressure and the residue treated with ethyl acetate until no more precipitation occurred; the ethyl acetate solution was dried, filtered, etc. The yield was 24 g. of sirup, which gave 16.65 g. of crystals (m. p. 81°) or 60% of the theoretical; m. p. of the phenylhydrazide, 103°.

(b) From 20 g. of crotonic acid, 23.7 g. of crude 2-methylglycidic acid was prepared as described under 2(b), and dissolved in 2 liters of water. After six weeks' standing at room temperature, the solution was worked up in the usual manner. The yield was 25.4 g. of a pale yellow sirup which gave 19.8 g. of crystals (m. p. 80.5–81°) from ethyl acetate, or 71% of the theoretical.

Oxidation of Crotonic Acid with Perbenzoic Acid in Non-aqueous Solution.—Twenty grams of crotonic acid was dissolved in 280 cc. of dry chloroform which contained 43 g. of perbenzoic acid. After about three months' standing in a cool place only a small amount of peracid was present; the bromine titration showed about 8 g. of unchanged crotonic acid. The chloroform was then removed at reduced pressure, the residue treated with 250 cc. of water and the benzoic acid separated and washed with water. The aqueous solution was distilled to dryness at reduced pressure, the residue 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.

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[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

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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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