2. The preparation of 3-bromocrotonic acid (m. p. 74°) is reported. This acid is prepared from 2-hydroxy-3-bromobutyronitrile in the same manner as in the case of 3-chlorocrotonic acid. The yield of acid, taking the nitrile as a basis, is about 12% of the theoretical.

A greatly improved method of preparation of dibromohydrin is reported. This product may be obtained now from glycerin with 54% yield.

The preparation of 2-hydroxy-3-bromobutyronitrile from dibromohydrin is described.

The preparation of ethyl 2-hydroxy-3-bromobutyrate (b. p. 94–96° at 2 mm.) and ethyl 3-bromocrotonate (b. p. 80° under 2 mm.) is reported.

3. The preparation of ethyl 3-iodocrotonate (b. p. 92–93° at 2 mm.) and that of the 3-iodo-crotonic acid (m. p. 108°) are described.

4. The structure of the 3-halogenocrotonic acids is proved. The 3-chloro acid may be reduced to crotonic acid (m. p. 72°); the 3-chloro- and 3-bromocrotonic acids may easily be converted into 3-iodocrotonic acid.

5. It is shown that the 3-chlorocrotonic acid is an intermediate product in the reduction of 3,3-dichlorocrotonic acid to crotonic acid.

6. An improved method of preparation of 3,3-dichlorocrotonic acid is described. The reduction of 3,3,3-trichlorocrotonic acid with zinc in acetic acid yields the 3,3-dichlorocrotonic acid in 80–85% yield.

CHICAGO, ILLINOIS

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

OXIDATION OF UNSATURATED COMPOUNDS. III. OXIDATION OF 3-CHLOROCROTONIC ACID. SYNTHESIS OF *dl*-THREONIC ACID. PROOF OF CONFIGURATION OF THE *dl*-1,2-DIHYDROXYBUTYRIC ACIDS

BY GÉZA BRAUN[1]

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In the study of hydroxylation of double bonds, undoubtedly fumaric and maleic acids have the most prominent place. Their structure was determined with a considerable degree of assurance[2] and the structure of their hydroxylated products—that of the tartaric acids—was proved with the greatest accuracy. Because the configurations of both starting and end products are known, it would be a comparatively simple matter to study the mechanism of the hydroxylation and the nature of the oxidizing agent in the oxidation of fumaric and maleic acids. Unfortunately these acids have a very inactive double bond. As a matter of fact it is possible to get satisfactory results only with the strongest hydroxylating agents,

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

[2] Although there might be objections, it is generally accepted that fumaric acid is the "*trans*" and maleic acid is the "*cis*" form.

such as potassium permanganate, and with osmic acid-activated chlorates. With these reagents fumaric acid always yields racemic acid and maleic acid always gives mesotartaric acid. The other group of hydroxylating agents—which would yield the ethylene oxide derivatives as intermediate products and which would give the tartaric acids isomeric with those obtained in the chlorate oxidations—cannot be used successfully in the oxidation of fumaric and maleic acids. These agents are hypochlorous acid and peracids. The reaction of hypochlorous acid with these acids was completely cleared up by Kuhn and Ebel,[3] but the reaction is very complicated and there does not seem to be any general rule in the oxidation, and the peracids, such as perbenzoic and peracetic acids, etc., proved to be unsuitable for the oxidation of fumaric and maleic acids.[3,4] In contrast to this, another pair of unsaturated acids—crotonic and isocrotonic acids—may easily be oxidized in such a manner that each of the isomeric acids, by application of different oxidizing agents, gives both of the theoretically possible *dl*-1,2-dihydroxybutyric acids in high yields.[4] To use the results of these oxidations as a basis of comparison in the study of the hydroxylation of double bonds, it was necessary to prove the configuration of the *dl*-1,2-dihydroxybutyric acids only, because the structure of the crotonic acids is known from Auwers and Wissebach's work.[5]

The proof of configuration of *dl*-1,2-dihydroxybutyric acids is presented in this paper. The proof is accomplished by an indirect method and is based on the fact that the *dl*-threo-1,2-dihydroxy-3-chlorobutyric acid may be converted into racemic acid through the intermediate formation of threonic acid; on the other hand, it may be reduced to the *dl*-1,2-dihydroxybutyric acid (m. p. 74–75°). This shows clearly that the *dl*-1,2-dihydroxybutyric acid (m. p. 74–75°) has the same configuration as racemic acid and the other possible acid—the *dl*-1,2-dihydroxybutyric acid (m. p. 81.5°) —must have a configuration corresponding to mesotartaric acid.

I. Oxidation of 3-Chlorocrotonic Acid

The 3-chlorocrotonic acid may be prepared now in 32% yield from the 2-hydroxy-3-chlorobutyronitrile.[6] The acid can be oxidized with osmic acid-activated chlorates to *dl*-threo-1,2-dihydroxy-3-chlorobutyric acid according to Hofmann's method,[7] modified by Milas and Terry.[8] The reaction proceeds just as well as in the case of fumaric or maleic acids. There is no change in the acidity during the oxidation; consequently no

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[3] Kuhn and Ebel, *Ber.*, **58,** 925 (1925).

[4] Böeseken, *Rec. trav. chim.*, **45,** 838 (1926); Géza Braun, THIS JOURNAL, **51,** 228 (1929).

[5] Auwers and Wissebach, *Ber.*, **56,** 715 (1923)

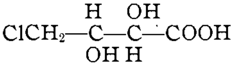
[6] Géza Braun, THIS JOURNAL, **52,** 3167 (1930).

[7] Hofmann, Ehrhart and Schneider, *Ber.*, **46,** 1657 (1914).

[8] Milas and Terry, THIS JOURNAL, **47,** 1412 (1925).

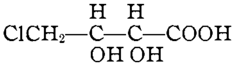
addition of hypochlorous acid to the double bond occurs as it does in the case of crotonic and isocrotonic acids.[4] As there is no formation of oxalic or volatile acids, it was concluded that no side reaction whatsoever occurred. The yield of oxidized, pure product (m. p. 97–98°) is as high as 75–78% of the theoretical. The purest product melts at 100°.

The analytical data indicate a formula $C_4H_7O_4Cl$. Considering the method of preparation of this compound, there are two possibilities for its structure



$$ClCH_2—\underset{OH}{\overset{H}{C}}—\underset{H}{\overset{OH}{C}}—COOH$$

I. *dl*-Threo-1,2-dihydroxy-3-chlorobutyric acid, or, briefly, 3-chlorothreonic acid



$$ClCH_2—\underset{OH}{\overset{H}{C}}—\underset{OH}{\overset{H}{C}}—COOH$$

II. *dl*-Erythro-1,2-dihydroxy-3-chlorobutyric acid, or 3-chloro-erythronic acid

Assuming that there is no inversion in the chlorate oxidations, the formula I would be expected to be correct. This was definitely proved by conversion of the compound into the racemic acid by oxidation with dilute nitric acid. Because the chloro compound cannot be oxidized directly, it was necessary first to remove the chlorine with silver acetate and then to oxidize the resulting product with nitric acid. The oxidation yielded, except for a small amount of oxalic acid, exclusively racemic tartaric acid. As the above reaction does not involve the asymmetric carbon atoms, no change in configuration can be assumed in this procedure and the oxidation definitely proves that the compound has the formula I.

The 3-chlorothreonic acid in all its reactions closely resembles the chlorohydroxy acids obtained from unsaturated acids by addition of hypochlorous acid. The organic chlorine is rapidly ionized in alkaline solution and the compound is converted into an ethylene oxide compound. In this case only one of the two asymmetric carbon atoms is involved in the reaction, whereas for instance in the case of the 1-chloro-2-hydroxybutyric acids the reaction takes place between both of the asymmetric carbon atoms. A comparison of these reactions offers interesting conclusions in regard to their mechanism. Work on these reactions is now in progress.

II. Synthesis of *dl*-Threonic Acid

Among the sugar acids that have been thoroughly studied only the *dl*-threonic acid has been unknown up to the present time. Nef[9] reported a mixture of *dl*-threonic and erythronic acids—obtained from *l*-arabinose by alkali—but the pure *dl*-threonic acid could not be isolated.

The *dl*-threonic acid is prepared by treatment of *dl*-threo-1,2-dihydroxy-3-chlorobutyric acid with silver oxide. According to this procedure the *dl*-threonic acid is obtained in 46% yield as a *free acid* (m. p. 98°). The acid according to analysis has a formula corresponding to $C_4H_8O_5$. Its configuration was proved by oxidation to racemic tartaric acid in the usual manner.

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[9] Nef, *Ann.*, **357**, 233 (1907).

Thus both of the theoretically possible *dl*-tetronic acids are known. The main difference between the two acids is that the *dl*-threonic acid does not form a lactone under the conditions in which the erythronic acid can be isolated only as a lactone. The characteristic derivatives of *dl*-threonic acid will be reported separately. The acid will be studied with special attention because of the fact that the *l*-threonic acid, which was thoroughly investigated by Anderson,[10] was reported as a lactone.

III. Proof of Configuration of *dl*-1,2-Dihydroxybutyric Acids

As was mentioned before, the *dl*-threo-1,2-dihydroxy-3-chlorobutyric acid has a prominent place as it makes a connection between the 1,2-dihydroxybutyric and the tartaric acids. After its configuration had been determined by conversion into racemic tartaric acid, it was only necessary to reduce the acid to one of the two theoretically possible 1,2-dihydroxybutyric acids in order to find which of these has the configuration corresponding to racemic acid.

The reduction was accomplished by palladium and hydrogen in the presence of alkali. The result of the reduction was the *dl*-1,2-dihydroxybutyric acid (m. p. 74°). Unfortunately the alkali causes a side reaction by formation of ethylene oxide compound, which lowers the yield of the desired product to about 50%, when all of the necessary sodium hydroxide is added at once. However, by gradual addition of sodium hydroxide during the reduction, it is possible to raise the yield of *dl*-1,2-dihydroxybutyric acid (m. p. 74°) to 70% of the theoretical. The reduction of the 3-chlorothreonic acid in acid solution has been thus far unsuccessful.

Bearing in mind that the result of reduction in alkaline solution is a *dl*-1,2-dihydroxybutyric acid, there are two possibilities for the course of the reaction: (1) the 3-chlorothreonic acid may be reduced directly to the dihydroxybutyric acid, or (2) the reduction may go through the ethylene oxide compound. In the latter case one of the asymmetric carbon atoms would be involved in the reaction and there would be a possibility of uncontrollable inversion, which would made the result indecisive. Although this is very improbable, a control reduction was made as follows: the 3-chlorothreonic acid was treated first with alkali in order to convert it into the ethylene oxide compound, and then this solution was added to an aqueous suspension of palladium on charcoal in a hydrogen atmosphere. The reduction proceeded in this case extremely slowly; the reaction mixture took up one molecule of hydrogen in about forty hours, whereas the direct reduction of the 3-chlorothreonic acid required only three to four hours. From the reduction product only about 15% of impure crystals of *dl*-1,2-dihydroxybutyric acid (m. p. 74°) was obtained. The great difference in the duration of the reduction and the quantity of acid obtained

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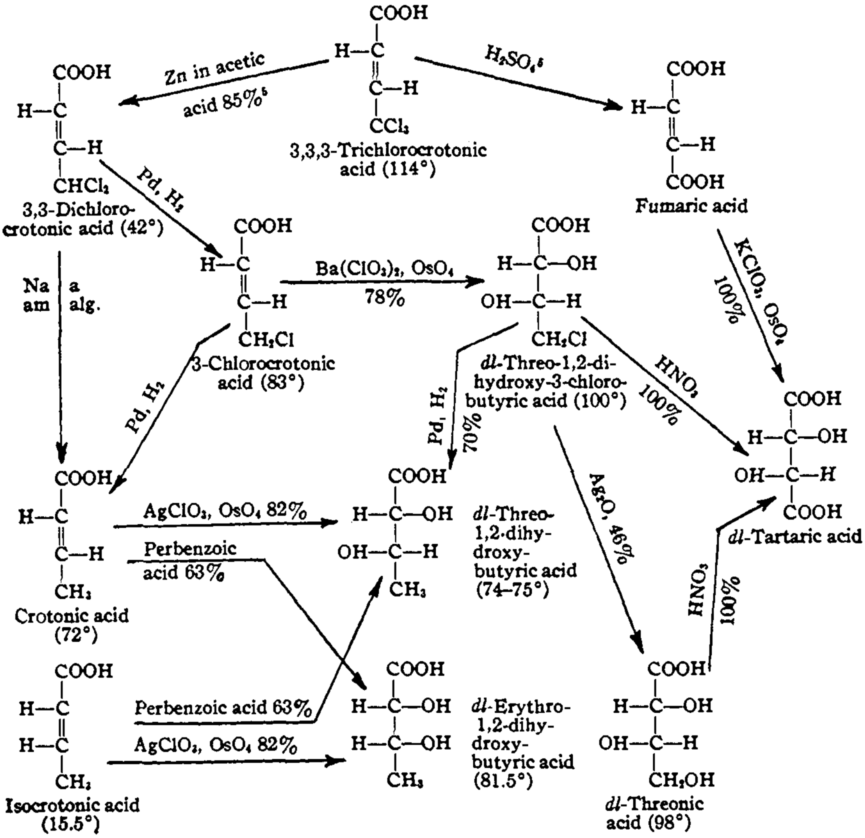
[10] Anderson, *Am. Chem. J.*, **42**, 425 (1909).

strongly supports the idea that Reaction 1 took place, and hence the asymmetric carbon atom was not involved in the reaction. It may be said, therefore, that the configuration of *dl*-1,2-dihydroxybutyric acid (m. p. 74°) corresponds to the racemic acid and that of *dl*-1,2-dihydroxybutyric acid (m. p. 81.5°) to the mesotartaric acid.

These results are a complete confirmation of the predictions made in a former publication.[4] In order to put an end to the last doubts on this subject, the reactions of 3-bromothreonic and 3-iodothreonic acids will be studied. These acids undoubtedly have much more active halogens and will be reducible in acid solution. Work on these reactions is in progress.

A general summary of all the reported reactions and the connection between the unsaturated and hydroxylated acids is shown in the chart.



Thus the structure of the *dl*-1,2-dihydroxybutyric acids having been established, the oxidation of crotonic and isocrotonic acids may be used as a basis of comparison in the study of hydroxylation of double bonds and especially for the study of the nature of any oxidizing agent. The final experimental data necessary to this purpose are supplied by the accomplishment of the separation of these acids from each other. The separation is based on the fact that the sodium salt of the "erythro" acid is about fifteen times as soluble in hot absolute alcohol as the corresponding salt of the "threo" acid. The separation is almost quantitative.[11]

Experimental Part

Materials

Palladium Catalyst.—The catalyst was prepared by precipitating palladium on charcoal in the usual manner. The apparatus used in the reduction was a calibrated pyrex tube of suitable size which was connected with the reaction flask—a 250-cc. suction flask—and a leveling bulb. The reaction flask was connected with a dropping funnel and a Y-tube for the addition of any solution necessary during the reduction. The reaction flask was violently shaken on a shaking machine. For the neutralization of the organic and hydrochloric acids the purest sodium hydroxide (made from metallic sodium) was used. In this manner it was possible to use the palladium catalyst many times without any loss of catalytic power.

Oxidation of 3-Chlorocrotonic Acid.—One hundred and twenty grams of 3-chlorocrotonic acid (m. p. 81.5°) was dissolved (partially suspended) in 1.5 liters of water which contained 0.5 g. of osmic acid and 60 g. of barium chlorate and the mixture was allowed to stand at room temperature. The mixture was frequently shaken at the beginning and cooled if the temperature rose over 30°. In about four to five hours all of the acid went into solution and in twenty hours all of the chlorate was used up and the solution became black. Then 4 g. of chlorate was added and the solution again allowed to stand for eighteen hours. The clear solution was now extracted twice with 500 cc. of benzene and the aqueous solution concentrated at reduced pressure (temperature of the bath not over 50°) to a thin sirup, which was dissolved in absolute alcohol and the solvent again removed at reduced pressure until the residue became a thick sirup. This was dissolved in about 1.5 liters of ether, when all of the inorganic matter precipitated and the solution became clear. The ethereal solution was thoroughly dried with much sodium sulfate, etc., as usual. The residue of the ethereal filtrate was a thick, colorless sirup which soon crystallized to a semi-crystalline mass. This was dissolved in about 100 cc. of warm ethyl acetate and, after addition of 50 cc. of chloroform, cooled to −15°. The crystals were separated by filtration and washed with a cold mixture of 25% ethyl acetate and 75% chloroform (by volume). The mother liquor of the crystals was concentrated at reduced pressure and the crystallization was repeated as above. After three successive crystallizations there was obtained 109 g. of crystals (m. p. 97–98°). The residue was now dissolved in 500 cc. of ether, filtered and the residue of the ethereal filtrate dissolved in 75 cc. of ethyl acetate–chloroform mixture. In two hours' standing at −15°, 7 g. of crystals was obtained making a total of 116 g. or 75% of the theoretical.

When the oxidation was made with gradual addition of barium chlorate and the excess of the barium chlorate was reduced with sulfur dioxide, etc., just as in the case of the oxidation of crotonic acid with chlorates, the desired product was obtained in 78% yield. There was no change in the acidity during the oxidation.

The crude crystals were recrystallized from 250 cc. of hot ethyl acetate and yielded in two crops a total of 105 g. of crystals (m. p. 100°). The residue of the mother liquor was a crystalline mass.

Titration. Subs., 0.2870, 0.4308: 18.1, 27.4 cc. of 0.1 *N* alkali for free acid; 18.47, 27.5 cc. of 0.1 *N* alkali and 18.5, 27.5 cc. of 0.1 *N* silver nitrate for organically bound

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[11] Glattfeld and Braun, unpublished results.

chlorine after saponification on the water-bath for fifteen minutes. Calcd. for $C_4H_7O_4Cl$: mol. wt., 154.52; Cl, 22.95. Found: mol. wt., 158.6, 157.2; Cl, 22.85, 22.64.

Anal. Subs., 0.005875: CO_2, 0.006817; H_2O, 0.002388. Calcd. for $C_4H_7O_4Cl$: C, 31.06; H, 4.57. Found: C, 31.64; H, 4.55. Subs., 0.4223: 27.0 cc. of 0.1 *N* silver nitrate (after treatment with sodium in absolute alcohol). Calcd. for $C_4H_7O_4Cl$: Cl, 22.95. Found: Cl, 22.67.

The substance is very soluble in water, acetone, ether, hot ethyl acetate, etc., moderately soluble in cold ethyl acetate, insoluble in chloroform and benzene.

Oxidation of 3-Chlorothreonic Acid with Nitric Acid.—Three and one-tenth grams of the acid was dissolved in 50 cc. of water and after addition of 5 g. of silver acetate the mixture was heated for ten hours at 60° with frequent shaking. The filtrate from the silver chloride, from which the excess silver was quantitatively removed with hydrochloric acid, was concentrated at reduced pressure to a thick sirup. This was dissolved in 15 cc. of nitric acid (sp. gr. 1.21) and the solution kept at 55° for fifty-six hours. Then the nitric acid was removed at reduced pressure in the usual manner and the white crystalline residue dissolved in the necessary amount of 20% potassium hydroxide. After neutralization of this solution, 1.5 cc. of glacial acetic acid was added, whereupon the potassium acid tartrate crystallized immediately; 2.65 g. of crude crystals was obtained, which gave 2.1 g. of pure crystals (dried at 100°) from 70 cc. of water.

Anal. Subs., 0.5036: 26.28 cc. of 0.1 *N* alkali. Calcd. mol. wt. for $C_4H_5O_6K$: 188.1. Found: 191.6.

0.5036 g. of potassium acid tartrate gave 0.66 g. of air-dried calcium tartrate.

Anal. Subs., 0.6570: loss in weight at 180°, 0.1812; ash, 0.1425. Calcd. for $C_4H_4O_6Ca{\cdot}4H_2O$: H_2O, 27.70. Found: H_2O, 27.58. Calcd. for $C_4H_4O_6Ca$: CaO, 29.81. Found: CaO, 29.94.

The filtrate from the potassium acid tartrate was diluted to 200 cc. and the oxalic acid was precipitated with a small amount of calcium acetate in the hot; 0.2 g. of calcium oxalate was obtained.

Anal. Subs., 0.2079: CaO, 0.0803. Calcd. for $CaC_2O_4{\cdot}H_2O$: CaO, 38.34. Found: CaO, 38.62.

The filtrate from the calcium oxalate, after addition of more calcium acetate, deposited 0.3 g. of crystals; reprecipitated, 0.23 g.

Anal. Subs., 0.2245: loss in weight, 0.0605 (at 180°); ash, 0.0496. Calcd. for $C_4H_4O_6Ca{\cdot}4H_2O$: H_2O, 27.70. Found: H_2O, 26.95. Calcd. for $C_4H_4O_6Ca$: CaO, 29.81. Found: CaO, 30.2.

Treatment of 3-Chlorothreonic Acid with Silver Oxide; Preparation of *dl*-Threonic Acid.—Twenty grams of the 3-chlorothreonic acid was dissolved in 200 cc. of water and neutralized with barium carbonate at low temperature. After the carbon dioxide was removed at reduced pressure, the solution was filtered and in the course of about fifteen hours freshly precipitated silver oxide from 23 g. of silver nitrate was added very slowly at 30–35° while the solution was violently stirred. Then the precipitate was removed by filtration and the filtrate treated with silver oxide again until the solution did not contain any more organic chlorine. This was the case after about twenty hours' stirring. (The temperature at the end of the reaction was about 40°.) Then the barium and silver were quantitatively removed in the usual manner.

One tenth of the filtrate (corresponding to 2 g. of 3-chlorothreonic acid) was concentrated to dryness and the residue was oxidized with dilute nitric acid as previously described. One gram of pure recrystallized potassium acid tartrate, 0.24 g. of calcium oxalate and 0.18 g. of calcium racemate (27.25% H_2O, 30.5% CaO) were obtained.

No trace of mesotartaric acid was found, proving that the treatment with silver oxide did not cause any inversion.

The remaining portion of the filtrate (18 g. of 3-chlorothreonic acid) was concentrated to dryness and the residue dried for four hours under 2 mm. pressure at 40°. Thus 14.7 g. of colorless sirup was obtained. This sirup crystallized spontaneously in about twelve hours. It was found to be more practical to dissolve the sirup in 25 cc. of acetone before the crystallization and then seed the solution with the crystals. The crystallization started immediately: 7.15 g. of white crystals was obtained. Recrystallization from absolute alcohol yielded 3.1 g. of crystals (m. p. 98°).

Titration. Subs., 0.3000, 0.2054 (from different preparations): 20.45 (directly) +0.55 (after heating), 14.65 + 0.14 cc. of 0.1 *N* alkali. Calcd. for $C_4H_8O_5$: mol. wt., 136.06. Found: mol. wt., 142.8, 138.9.

Anal. Subs., 0.003876, 0.003884 (from different preparations): H_2O, 0.002094, 0.00205; CO_2, 0.005109, 0.00514. Calcd. for $C_4H_8O_4$: H, 5.93; C, 35.3. Found: H, 6.04, 5.90; C, 35.94, 36.1.

One gram of the crystals (m. p. 98°) was dissolved in 6 cc. of nitric acid (sp. gr. 1.21) and the solution kept at 56° for fifty hours, etc., as is described in the case of 3-chlorothreonic acid. The white, crystalline oxidation product gave 0.95 g. of recrystallized potassium acid tartrate.

Titration. Subs., 0.5200: 27.18 cc. of 0.1 *N* alkali. Calcd. mol. wt. for $C_4H_5O_6K$: 188.1. Found: mol. wt., 191.3.

Fifty-two hundredths of a gram of potassium acid tartrate gave 0.7 g. of calcium tartrate (air dried).

Anal. Subs., 0.6760: loss in weight at 180°, 0.1852; ash, 0.1468. Calcd. for $C_4H_4O_6Ca \cdot 4H_2O$: H_2O, 27.70. Found: H_2O, 27.40. Calcd. for $C_4H_4O_6Ca$: CaO, 29.81. Found: CaO, 29.91.

The filtrate from the potassium acid tartrate gave 0.05 g. of calcium oxalate (CaO, 38.12; calcd., 38.34) and 0.07 g. of calcium tartrate (H_2O, 27.48; CaO, 30.03). No mesotartaric acid was found.

The *dl*-threonic acid was obtained therefore as a free acid (m. p. 98°). It is very soluble in water, in hot glacial acetic acid, in hot absolute alcohol; insoluble in acetone or ethyl acetate.

Reduction of 3-Chlorothreonic Acid with Palladium and Hydrogen. (a) **Sodium Hydroxide Added in One Operation.**—Three and one-tenth grams of 3-chlorothreonic acid was dissolved in 40 cc. of water and cooled in a freezing mixture until much ice appeared. Then gradually, under effective cooling, 40 cc. of 1 *N* sodium hydroxide and 5 g. of palladium-norit (corresponding to 0.1 g. of palladium) was added. The temperature during the neutralization should never rise above − 1°. Then the mixture was violently shaken in a hydrogen atmosphere. The operation must be carried out as quickly as possible and the temperature must be very low at the beginning. The reduction was practically complete in two hours but it was continued for four hours, when no more hydrogen was taken up. The reaction mixture took up approximately the theoretical amount of hydrogen (the hydrogen necessary for the saturation of palladium-norit—in this case about 180 cc.—must be taken into account). The materials from three experiments were united (9.3 g. of 3-chlorothreonic acid); to the filtrate of the palladium-norit, which contained the theoretical amount of sodium chloride, 57 cc. of 1 *N* sulfuric acid was added and the solution concentrated to a thick sirup at reduced pressure. The residue was dried completely at 40° under 2 mm. pressure and extracted several times with hot ethyl acetate (altogether 250 cc.). The residue of ethyl acetate solution weighed 4.0 g. (55% of theoretical); this crystallized after considerable warming when the walls of the flask were scratched. The hard crystalline mass gave 3 g. of crystals (m. p. 73–74°) from ethyl acetate. The mother liquor of these crystals deposited crystals again at 0°, showing the purity of the starting product. For identification see below under (b). The residue of the ethyl acetate extraction was treated with absolute alcohol. Three grams of a pale yellow sirup was obtained, which would not crystallize.

(b) **Reduction with Gradual Addition of Sodium Hydroxide.**—Three and one-tenth grams of 3-chlorothreonic acid was dissolved in 60 cc. of water, neutralized with 20 cc. of 1 *N* sodium hydroxide below 0° as under (a) and after addition of 10 g. of palladium–norit (0.2 g. of palladium) the mixture was violently shaken in hydrogen atmosphere in the apparatus previously described. After half an hour, when the solution was saturated with hydrogen, 22.5 cc. of 1 *N* sodium hydroxide was added very slowly in about three hours. The mixture was shaken for two hours further, when approximately the theoretical amount of hydrogen was taken up. The products of two experiments were united (6.2 g. of 3-chlorothreonic acid) as under (a). The residue of the ethyl acetate solution, which crystallized at once to a hard crystalline mass, weighed 3.4 g. (70% of the theoretical) dried over phosphorus pentoxide under 2 mm. pressure. From this, 2.9 g. of crystals (m. p. 74°) was obtained in two crops (60% of the theoretical). The filtrate from the crystals (0.4) still deposited crystals.

A mixed melting point of the product with pure *dl*-1,2-dihydroxybutyric acid (m. p. 74–75°) was 74°.

One gram of this product was dissolved in 10 cc. of absolute alcohol and 0.9 cc. of phenylhydrazine was added; 1.6 g. of hydrazide was obtained which yielded, after recrystallization from absolute alcohol, 1.25 g. of crystals (m. p. 132–133°); a mixed melting point with the phenylhydrazide of *dl*-1,2-dihydroxybutyric acid was 132–133°.

Anal. Subs., 0.00456: N_2, 0.49 cc. (23.5°, 742 mm.). Calcd. for $C_{10}H_{14}O_3N_2 \cdot H_2O$: N, 12.28. Found: N, 12.30.

(c) **Reduction of 3-Chlorothreonic Acid after Treatment with Sodium Hydroxide.**—Three and one-tenth grams of 3-chlorothreonic acid was dissolved in 20 cc. of water and treated with 42 cc. of 1 *N* sodium hydroxide below 0° as described before. The solution was allowed to stand for three hours at −1°; then for two hours at room temperature. By this time 94–95% of the organic chlorine was ionized. This solution was now added to an aqueous suspension of 10 g. of palladium–norit (0.2 g. Pd)—which had been previously saturated with hydrogen—and the mixture was shaken in a hydrogen atmosphere. The theoretical amount of hydrogen (one mol) was taken up in about forty hours. The reaction mixture was worked up as under (a). The residue of ethyl acetate solution (1.6 g.) deposited impure crystals at −15° (about 0.6–0.7 g.) which gave 0.3 g. of crystals (m. p. 68°) from ethyl acetate. This product undoubtedly contained a large percentage of *dl*-1,2-dihydroxybutyric acid (m. p. 74°), formed by the reduction of unchanged 3-chlorothreonic acid which remained after the sodium hydroxide treatment.

The author wishes to thank Dr. J. Stieglitz for valuable suggestions, Dr. J. W. E. Glattfeld for help in the prosecution of this work and the International Education Board for partial financial support.

Summary

1. The oxidation of 3-chlorocrotonic acid (m. p. 83°) with barium chlorate is reported. The oxidation yields the *dl*-threo-1,2-dihydroxy-3-chlorobutyric acid (m. p. 100°) in 78% yield. The structure of the hy-

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.

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

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

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

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