Summary

1. Convenient methods for making allyl halides are described. Allyl bromide and allyl chloride made in this way do not develop objectionable odors and colors on standing.

2. Sulfuric acid is to be condemned in the preparation of pure alkyl halides.

3. In the preparation of pure alkyl halides, even by the Norris method, a small amount of unsaturated materials is formed.

4. Sulfuric acid not only polymerizes these materials but attacks sensitive halides to form more unsaturated materials.

5. The colors of decomposing halides are caused by the action of sulfuric acid and halogen acid on the unsaturated materials.

6. The Norris procedure gives the purest products.

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

OXIDATION OF UNSATURATED COMPOUNDS.
I. OXIDATION OF CROTONIC AND ISOCROTONIC ACIDS, OF THE LACTONE OF 3-HYDROXY-ISOCROTONIC ACID AND OF MALEIC ANHYDRIDE

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I. Oxidation of Crotonic and Isocrotonic Acids

According to the van't Hoff-Wislicenus theory there are two isomeric 2-methylacrylic acids, the *cis* and *trans*. In the opinion of Auwers[2] the *cis* form represents *iso*crotonic and the *trans* form crotonic acid. Since this pair of acids has active double bonds and has been thoroughly studied from the point of view of *cis-trans* isomerism, these acids are very well suited for the study of the addition of hydroxyl groups.

Several different methods for the oxidation of crotonic acid are reported in the literature. Melikoff[3] oxidized it with hypochlorous acid and prepared a dihydroxybutyric acid (m. p. 80°) through the intermediate formation of 2-methylglycidic acid. Fittig and Kochs[4] used barium permanganate, Glattfeld and Woodruff[5] potassium chlorate; in both cases the identical dihydroxybutyric acid, m. p. 74–75°, was obtained.

The pure, crystallizable *iso*crotonic acid had not previously been used for oxidation. Melikoff and Petrenko-Kritschenko[6] succeeded in pre-

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[1] International Research Fellow in Organic Chemistry from Hungary.

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

[3] Melikoff, *Ann.*, **234**, 197 (1886).

[4] Fittig and Kochs, *ibid.*, **268**, 7 (1892).

[5] Glattfeld and Woodruff, This Journal, **49**, 2309 (1927).

[6] Melikoff and Petrenko-Kritschenko, *Ann.*, **266**, 359 (1891).

paring crystallized dihydroxybutyric acid (m. p. 45°) by the oxidation of Geuther's[7] crude *iso*crotonic acid, which contained crotonic and tetrolic acids.[8] Fittig and Kochs[4] and later Morrell and Bellars[9] failed to get crystallized products with barium permanganate. They obtained only sirups which did not crystallize or which occasionally contained a few crystals.

The whole situation was rather confused in many respects. The yields of pure dihydroxybutyric acids were cut down by side reactions and isomerizations to such an extent that they were not higher than 20–25%. It was therefore necessary to work out new methods which would show the relation between the crotonic acids and the dihydroxybutyric acids and which would give sufficiently high yields for the study of the addition of hydroxyl groups.

This paper is a report of (A) **perbenzoic acid oxidations** of crotonic and *iso*crotonic acids for the *trans* addition of the hydroxyl groups. The method gave a yield of 63% of dihydroxybutyric acids from both crotonic and *iso*crotonic acids. (B) **Chlorate oxidations** of these two acids for the *cis* addition of the hydroxyl groups. The yields were as high as 82% in both cases.

(A) Oxidations by Means of Perbenzoic Acid

(a) **Oxidation of Crotonic Acid (m. p. 72°).**—In one of his recent papers, Böeseken[10] states that crotonic acid cannot be oxidized with perbenzoic acid. Although the reduction of the per-acid is so very slow as to be easily overlooked, as a matter of fact the oxidation of crotonic acid proceeds very well in both aqueous and non-aqueous solutions.

Among the various methods for the oxidation in the presence of water, Bergmann's[11] method was found to be the best: crotonic and perbenzoic acids were dissolved in chloroform and this solution was shaken with much water. The oxidation takes place in the chloroform phase and the water removes the oxidized product immediately. The yield was about 88% of a viscous sirup which yielded from ethyl acetate 63–64% of crystals, m. p. 81.5°. This product was a dihydroxybutyric acid. Its melting point did not change when the substance was mixed with the acid obtained by the oxidation of *iso*crotonic acid with silver chlorate (see later). The molecular weight, according to titration, was 121. This corresponds to a formula $C_4H_8O_4$.

The mother liquor from the crystals melting at 81.5° was a non-crystallizable sirup. According to titration it was a mixture of the dihydroxy-

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[7] Geuther, *Z. Chem.*, 242 (1871).

[8] Michael and Schulthess, *J. prakt. Chem.*, [2] **46**, 248 (1891).

[9] Morrell and Bellars, *J. Chem. Soc.*, **85**, 350 (1904).

[10] Böeseken, *Rec. trav. chim.*, **45**, 838 (1926).

[11] Bergmann and Schotte, *Ber.*, **54**, 440, 1564 (1921).

butyric acid and perhaps its lactide. Probably both of the theoretically possible *dl*-1,2-dihydroxybutyric acids were present. As there is at present no known method for the separation of these acids or their derivatives, the sirup was not further investigated.

It is an interesting fact that crotonic acid even in pure water solution can be oxidized with perbenzoic acid. However, the yields were not higher than 30–40% of crystallized product, m. p. 81.5°, when either concentrated or diluted solutions of the per-acid were used.

(b) **Oxidation of Isocrotonic Acid (m. p. 15.5°).**—The oxidation was carried out under conditions which had been found to be most favorable in the treatment of crotonic acid. The yield of crude product was 90% of the theoretical; that of crystalline product, m. p. 74–75°, was 62–63% of the theoretical. A mixture of this acid (75°) with the acid obtained by the oxidation of crotonic acid with chlorate (75°) showed no depression of the melting point.

The oxidation of *iso*crotonic acid in aqueous solution was more successful than that of crotonic acid but very slow. The yield of dihydroxybutyric acid, m. p. 74°, was about 65% of the theoretical.

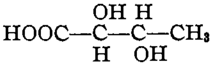
The oxidation of both crotonic and *iso*crotonic acids in non-aqueous solution is now in progress.

Discussion of the Results

The perbenzoic acid oxidation of crotonic acid gave a dihydroxybutyric acid, m. p. 81.5°, which is identical with the acid obtained from *iso*crotonic acid by oxidation with chlorate and which must be the same as Melikoff's acid, m. p. 80°.

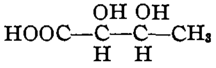
The perbenzoic acid oxidation of *iso*crotonic acid gave a dihydroxybutyric acid, m. p. 74–75°; this is the same acid that was obtained from crotonic acid with chlorates and permanganate.[5]

According to theory there are two *dl*-1,2-dihydroxybutyric acids. It is suggested that the prefixes *threo* and *erythro* be attached to the names of these substances to distinguish them and to show their relations to the well known threonic and erythronic acids



$$\mathrm{HOOC{-}\underset{H}{\overset{OH}{C}}{-}\underset{OH}{\overset{H}{C}}{-}CH_3}$$

dl-threo-1,2-Dihydroxybutyric acid



$$\mathrm{HOOC{-}\underset{H}{\overset{OH}{C}}{-}\underset{H}{\overset{OH}{C}}{-}CH_3}$$

dl-erythro-1,2-Dihydroxybutyric acid

One of these dihydroxybutyric acids melts at 74–75°, the other at 81.5°; but which of these is the *threo* form and which the *erythro* form cannot be decided so satisfactorily as in the case of the tartaric acids, where one form is internally compensated and the other is not. However, if the configuration of the crotonic acids is assumed[2,12] and advantage is taken of the experience of other workers in regard to the manner of addition of hydroxyl

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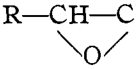
[12] For objection see Kuhn and Ebel, *Ber.*, **58**, 925 (1925).

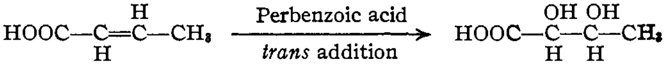
groups at a double bond, it is possible to assign configurations to the two acids in question with a considerable degree of assurance.

It has been shown[11,13] many times that in the oxidation by perbenzoic acid the first step is the formation of an ethylene oxide ring,  $R{-}\underset{\diagdown O \diagup}{CH{-}CH}{-}R$.[2] In the presence of water this ring opens and the compound is converted into the 1,2-glycol. In both steps there is a possibility of formation of both *cis* or *trans* compounds.

The oxidation of crotonic and *iso*crotonic acids with perbenzoic acid gave the dihydroxybutyric acids, isomeric with those obtained in the chlorate oxidations; that is, crotonic acid with perbenzoic acid yielded the *dl*-1,2-dihydroxybutyric acid, m. p. 81.5°, and with silver chlorate the *dl*-1,2-dihydroxybutyric acid, m. p. 75°. Assuming that the configurations ordinarily assigned to maleic and fumaric acids are correct, then it may be said that no case of inversion has ever been observed in a chlorate oxidation. On later pages of this paper will be found evidence supporting this statement. Hence the acid obtained by oxidation with perbenzoic acid is not the same as the acid obtained by chlorate oxidation, and therefore the oxidation with perbenzoic acid must involve a *single* inversion—either *trans* formation or *trans* splitting of the ethylene oxide ring.

There is no work reported in the literature to show whether the *direct* formation of the ring by oxidation of a double bond is *cis* or *trans;* but the *trans* splitting of the ring in the presence of water seems very probable from the work of Böeseken.[14] According to Kuhn and Ebel,[12] this *trans* splitting of the oxide rings is a general occurrence and in one case it was definitely proved: the hydrolysis of the internally compensated *cis*-ethylene-oxide-dicarboxylic acid yielded exclusively racemic tartaric acid. The proof in this case is based on the optical properties of both starting and end products. It seems, therefore, to be free from objections. So it seems probable that in the perbenzoic acid oxidations there is a *cis* formation of the oxide ring and then, in the presence of water, a *trans* splitting of the ring; this means a *trans* addition of the hydroxyl groups to the double bond.

Now if it be assumed that the oxidations of crotonic and *iso*crotonic acids by perbenzoic acid run in the same way as in the cases cited, then the two reactions may be written as follows:



$$HOOC{-}\underset{H}{C}{=}\overset{H}{C}{-}CH_3 \xrightarrow[trans\ addition]{Perbenzoic\ acid} HOOC{-}\underset{H}{\overset{OH}{C}}{-}\underset{H}{\overset{OH}{C}}{-}CH_3$$

Crotonic acid, m. p. 72°

dl-erythro-1,2-Dihydroxybutyric acid, m. p. 81.5°

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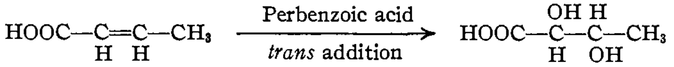
[13] Prileschajew, *Ber.*, **42,** 4811 (1909).

[14] Böeseken, *ibid.*, **56,** 2409 (1923).



$$\mathrm{HOOC{-}\underset{H}{C}{=}\underset{H}{C}{-}CH_3} \xrightarrow[\textit{trans}\text{ addition}]{\text{Perbenzoic acid}} \mathrm{HOOC{-}\overset{OH}{\underset{H}{C}}{-}\overset{H}{\underset{OH}{C}}{-}CH_3}$$

*Iso*crotonic acid, m. p. 15.5° *dl-threo*-1,2-Dihydroxybutyric acid, m. p. 74–75°

This means that the acid of m. p. 74–75° is the *threo* form and the acid of m. p. 81.5° is the *erythro* form.

(B) Oxidation of Crotonic and Isocrotonic Acids with Barium and Silver Chlorates with Osmic Acid as a Catalyst

(a) **Oxidation of Crotonic Acid with Barium Chlorate.**—The oxidation of crotonic acid by means of potassium chlorate with osmic acid as catalyst was recently carried out by Glattfeld and Woodruff.[5,15] A more careful study of this oxidation showed that there was a strong decrease in the initial acidity. This must be due to side reactions, since simple addition of hydroxyl groups to crotonic acid would not change its total acidity, and lactone formation cannot be assumed in this case. In order to clarify the mechanism of this reaction barium chlorate was used instead of potassium chlorate because it may be removed quantitatively from the reaction mixture.

Even under the most favorable conditions used—when the oxidation was carried out in dilute solution at room temperature—there was found a decrease of about 24% in the total acidity after the oxidation was complete. After all of the inorganic matter had been removed, there was found to be a large amount of organically bound chlorine in the solution. This chlorine proved to be present as a chlorohydroxybutyric acid, the formation of which may be explained only by the addition of the *free* hypochlorous acid to the crotonic acid. This is also the reason for the decrease in the acidity; the decrease in acidity is directly proportional to the absorption of hypochlorous acid.[16]

In the most successful of the oxidation experiments carried out, about 20% of the crotonic acid was chlorinated, so that in the reaction mixture in these experiments there were present the dihydroxybutyric acid and chlorohydroxybutyric acid as chief products. The separation of the two acids was very simple: the water was completely removed by distillation at reduced pressure and the dihydroxybutyric acid was separated by crystallization from ethyl acetate as completely as possible. The mother liquor contained the chlorohydroxybutyric acid. The yield of dihydroxybutyric acid (m. p. 74°) was 38% of the theoretical.

The mother liquor was shaken two or three times with water in order to remove the rest of the dihydroxybutyric acid; the ethyl acetate was removed by distillation, leaving the crude chlorohydroxybutyric acid as a

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[15] Medwedew and Alexejewa, "Papers on Pure Appl. Chem. Karpow-Inst.," Moskau, **1927**, *Chem. Zentr.*, [2] 1012 (1927).

[16] Formation of lactides, of course, also decreases the acidity.

sirup which was identified by analysis but which could not be rendered crystalline. The crystallized acid (m. p. 76°) could be prepared only from the crystallized zinc salt. That this acid was a chlorohydroxybutyric acid was shown by analysis for chlorine and by titration. On account of the small quantity its structure could not be determined.

The addition of hypochlorous acid to crotonic acid in the oxidation experiments with chlorates is then a fact. This chlorination could not be avoided although the oxidation was carried out under various conditions. It was a little lower when the barium chlorate was added gradually during the oxidation and considerably lower (about 3%) when the neutral barium crotonate was oxidized. But the oxidation of barium crotonate is not a practicable method because it is extremely slow: after one year about 30% of the crotonic acid was still present under circumstances in which the oxidation in acid solution was complete in ten days. That the chlorate oxidations do not proceed in neutral solution was recently observed also by Milas.[17]

(b) **Oxidation of Crotonic Acid with Potassium Chlorate.**—The results of the oxidations with potassium chlorate were exactly the same as those with barium chlorate. A potassium-acid double salt was separated in this case as an intermediate product. According to analysis it had the approximate formula $C_4H_7O_4K \cdot C_4H_8O_4$. The product is very soluble in water and hot absolute alcohol, from which it may be recrystallized; it is insoluble in ethyl acetate. For identification it was dissolved in water and the calculated amount of sulfuric acid was added. The dihydroxybutyric acid (m. p. 74°) was obtained with 80% yield. The product was not further investigated.

(c) **Oxidation of Crotonic Acid with Silver Chlorate.**—We have just seen that oxidation with barium and potassium chlorates does not proceed without the simultaneous addition of hypochlorous acid, whether the free crotonic acid or barium crotonate is used. When silver chlorate was used, however, hypochlorous acid addition was reduced to a minimum. This advantage of the silver chlorate is due to the following facts. The silver chloride precipitates as soon as formed; the silver hypochlorite is a very unstable compound and decomposes immediately according to the equation $3AgOCl = AgClO_3 + 2AgCl$. The addition of the hypochlorous acid to the double bonds is therefore greatly reduced.

Two sets of experiments were carried out with silver chlorate: in one set the necessary amount of chlorate (30% excess over the theoretical) was added in one operation at the beginning of the oxidation; in the other set the chlorate was added gradually in order to keep its concentration during the oxidation as low as possible.

In the first set the yield of dihydroxybutyric acid (m. p. 74°) was about

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[17] Milas, THIS JOURNAL, **49**, 2010 (1927).

60% of the theoretical; about 5% of the crotonic acid was chlorinated under these conditions. The silver salt of the dihydroxybutyric acid (m. p. 74°) was separated as an intermediate product. This silver salt crystallized out when the purified water solution of the dihydroxy acid was concentrated at reduced pressure and could be isolated with absolute alcohol. (One should handle the alcoholic silver precipitates in the presence of chlorate very carefully.)

When the silver chlorate was gradually added in small portions (the second set), practically no chlorination occurred. The osmic acid itself was used as indicator for the course of the oxidation: when the silver chlorate was used up, the color of the solution became brown due to the formation of the lower oxides of osmium. The color disappeared in a short time (even at 0°) after addition of more chlorate. The yield of oxidized product was about 92% and that of crystallized product (m. p. 74°) 70% when the oxidation was carried out at room temperature. When the oxidation was carried out at 0°, the yield of desired product was almost quantitative. Only a small quantity of oxalic and volatile acids was formed. The yield of the crystallized dihydroxybutyric acid (m. p. 74°) was as high as 82% of the theoretical. Investigation of the non-crystallizable sirup—which contained a great deal of dihydroxybutyric acid—is now in progress.

A complete summary of the oxidations carried out with crotonic acid in 2% aqueous solution is given in Table I.

Table I

Summary of Oxidations

25% excess of chlorate used. Room temperature in first five, 0° in last

Chlorate of	Added	OsO_4 per 100 g. of crotonic acid, g.	Dur. of oxid., weeks	Decr. in init. acidity, %	Crotonic acid chlor., %	Yield of oxid. prod., %	Yield of di-OH-butyric acid (75°) %	Other crystalline products
Ba	At once	0.125	1	24	20	79	38	$C_4H_7O_3Cl$ (m. p. 76°)
Ba	Gradually	.25	4	24	20	89	48	$C_4H_7O_3Cl$ (m. p. 76°)
K	Gradually	.25	4	24	20	..	..	$C_4H_7O_4K$, $C_4H_8O_4$
Ag	At once	.25	1	7	5	90	60	$C_4H_7O_4Ag$
Ag	Gradually	.25	4	3	1.5	92	70	....
Ag	Gradually	.5	4	0	1.5	96	82	....

(d) **Oxidation of Isocrotonic Acid (m. p. 15°) with Silver Chlorate.**—The oxidation was carried out by the gradual addition of silver chlorate at 0° in exactly the same manner as with crotonic acid. The yield of oxidized product was 97%; this gave 82% of the theoretically possible amount of crystalline product (m. p. 81.5°). The mixture of this acid with the acid obtained by the oxidation of crotonic acid with perbenzoic acid showed no depression of the melting point.

II. Oxidation of the Lactone of the 3-Hydroxy-isocrotonic Acid with Silver and Barium Chlorates

The lactone was prepared by Lespieau[18] and oxidized with alkali chlorates by Glattfeld and Cohen[19] with good yield. The oxidation was repeated with silver and barium chlorates at room temperature. The yield of erythronic lactone (m. p. 89–90°) in the silver chlorate oxidations was as high as 75% of the theoretical; in the barium chlorate oxidation it was a little lower, 64% of the theoretical. The recrystallized erythronic lactone melted at 92°. For identification it was oxidized with dilute nitric acid according to Anderson[20] and yielded, except for a small amount of oxalic acid, exclusively mesotartaric acid.

In no case was there found any chlorinated compound; the lactone has a very inactive double bond and shows great resistance to the addition of hypochlorous acid.

III. Oxidation of Maleic Anhydride

The oxidation of maleic anhydride and of maleic and fumaric acids with perbenzoic acid was attempted under various conditions but in no case did oxidation occur. This agrees with the observation of Böeseken[10] and Kuhn.[12]

The oxidation of maleic anhydride with barium chlorate in dilute aqueous solution was as successful as that of maleic and fumaric acids described by Milas and Terry.[21] A great difference between the barium and silver chlorate oxidations was observed, while the oxidation with barium chlorate was almost quantitative; the oxidation with silver chlorate under the same conditions gave only a 70% yield of mesotartaric acid. The ratio of the yields with the two chlorates in question, when maleic and fumaric acids were oxidized, was found to be the same. Silver chlorate in these cases is therefore not suitable for the oxidations.

No chlorination was observed in the chlorate oxidations; maleic anhydride (as well as maleic acid in water solution) has an inactive double bond and adds hypochlorous acid only slowly in acid solution.

Discussion of the Results

Hofmann first used activated chlorates for the oxidation of unsaturated compounds.[22] He states that the action of chlorates on ethylene double bonds in the presence of osmic acid in neutral solution, in solutions slightly

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[18] Lespieau, *Bull. soc. chim.*, [3] **33**, 466 (1905); Glattfeld and Leavell, unpublished results.

[19] Glattfeld and Cohen, unpublished results.

[20] Anderson, *Am. Chem. J.*, **42**, 429 (1909).

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

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

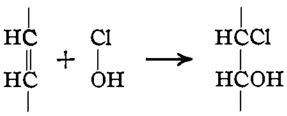
alkaline with bicarbonate or in weakly acid solutions, is exactly the same as that of potassium permanganate, and the reduction of chlorates to chlorides does not pass through the lower oxides of chlorine; the potassium chlorate is reduced directly to potassium chloride. So Hofmann writes the equation for the reaction as follows: $2OsO_4 = Os_2O_5 + 3O$ and $Os_2O_5 + KClO_3 = 2OsO_4 + KCl$.

Milas and Terry [21] recently investigated the oxidation of fumaric and maleic acids by alkali chlorates; they state that the principal reduction products of chlorate in the reaction are chlorite and chloride, principally the latter. The presence of traces of hypochlorous acid and free chlorine was shown by qualitative tests.

Now, the work on the oxidation of crotonic acid by chlorates reported in the present paper shows that: (1) when the crotonic acid is oxidized with barium or potassium chlorate—whether the chlorate is added at the beginning in one operation or added gradually during the oxidation—about 20% of the crotonic acid is chlorinated by the addition of hypochlorous acid; (2) if barium crotonate is oxidized in *neutral* solution, about 3% of the crotonic acid is chlorinated; (3) even in the presence of silver chlorate there occurs 5% chlorination, when the concentration of the silver chlorate is great; and (4) practically no chlorination occurs if the concentration of the silver chlorate is kept as low as possible.

As mentioned before, the addition of hypochlorous acid is an established fact. For the source of the hypochlorous acid which is added there are two possibilities.

1. **"Status nascens" Addition.**—According to the law of mass action, free chloric acid must be present when a metal chlorate is added to a water solution of an acid: $RCH{=}CHCOOH + MeClO_3 \rightleftarrows RCH{=}CHCOOMe + HClO_3$. The chloric acid will be reduced by the catalytic action of the osmic acid: $HClO_3 \longrightarrow HClO_2 \longrightarrow HClO$. When the reduction has proceeded to the hypochlorous acid stage, two reactions occur simultaneously: one part of the hypochlorous acid is further reduced to hydrogen chloride and another part adds "status nascens" to the double bond



$$\begin{array}{c} | \\ HC \\ \| \\ HC \\ | \end{array} + \begin{array}{c} Cl \\ | \\ OH \end{array} \longrightarrow \begin{array}{c} | \\ HCCl \\ | \\ HCOH \\ | \end{array}$$

If the concentration of the chloric acid, and therefore of the hypochlorous acid, is very low, then there is sufficient osmic acid present to reduce the hypochlorous acid almost completely, and the addition of the hypochlorous acid to the double bond will occur practically not at all. This may be the explanation of the fact that there was very little chlorination when the oxidation of crotonic acids was carried out with silver chlorate and when the concentration of the chlorate was kept as low as possible, while 5% chlorination occurred when the silver chlorate was used in excess.

2. **"Secondary" Addition.**—After a certain amount of chloric acid has been reduced to hydrogen chloride, these compounds react with the formation of chlorine: $HClO_3 + 5HCl \longrightarrow 3Cl_2 + 3H_2O \longrightarrow 3HCl + 3HClO$, and the hypochlorous acid thus formed adds to the double bond.

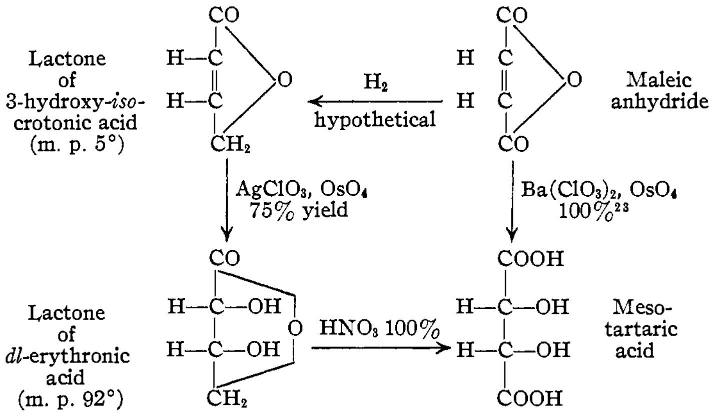
The chlorination of the neutral barium crotonate and chlorination in the presence of silver chlorate point to the "status nascens" source of the hypochlorous acid; in these cases the concentration of the hydrogen chloride is very low and the "secondary" source is not probable. However, if chlorates which give soluble chlorides, such as barium, potassium chlorate, etc., are used, then it is very probable that the hypochlorous acid added comes from both sources, for only a slight difference was observed when the crotonic acid was oxidized by the addition of barium chlorate in one operation at the beginning or by gradual addition of the barium chlorate throughout the oxidation. If the "status nascens" source of the hypochlorous acid were the only source, then in the latter case there would have been much less chlorination, just as in the case of silver chlorate oxidations; but the results of the oxidation with barium chlorate under the two sets of conditions were almost identical, showing that hypochlorous acid was produced by both methods.

In conclusion, it seems to be very probable that in every case the reduction of chlorates passes through the lower oxides of chlorine and some of the hypochlorous acid added is generated by the "status nascens" process; and not only in strong acid solution, as Hofmann stated, but even in weakly acid solution, there is a reaction between the chloric and hydrochloric acids with the formation of hypochlorous acid.

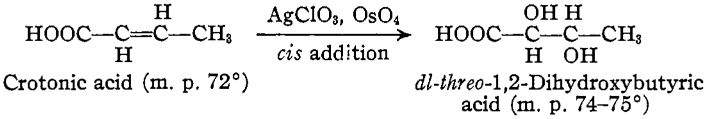
The mechanism of the catalytic action of osmic acid will not be treated at the present time.

The Manner of Addition of Hydroxyl Groups to Double Bonds in Chlorate Oxidations

It has been shown many times in the literature that in the case of chlorate oxidations with osmic acid—when an unsaturated compound was oxidized—just as in case of potassium permanganate oxidations, there is a *cis* addition of the hydroxyl groups. Milas and Terry[21] improved Hofmann's method and obtained an almost quantitative yield when fumaric acid was oxidized to *racemic* tartaric acid and maleic to mesotartaric acid, and, recently, Glattfeld and Cohen oxidized "maleic"—the lactone of 3-hydroxy-*iso*crotonic acid, to *dl*-erythronic lactone. All of the above oxidations were now repeated but under the same conditions that were used with crotonic acid; the results of these experiments are given below and show that the addition of the hydroxyl groups is *cis*.



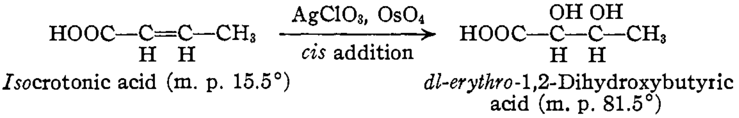
The silver chlorate method of oxidation of crotonic acid yielded *dl*-1,2-dihydroxybutyric acid (m. p. 74–75°) and *iso*crotonic acid yielded by the same method *dl*-1,2-dihydroxybutyric acid (m. p. 81.5°). Now if it is assumed that the oxidations of crotonic and *iso*crotonic acids proceed in the same way as in the former cases, these reactions may be indicated as follows



$$\mathrm{HOOC{-}\underset{H}{C}{=}\overset{H}{C}{-}CH_3} \xrightarrow[cis\ \mathrm{addition}]{\mathrm{AgClO_3,\ OsO_4}} \mathrm{HOOC{-}\underset{H}{\overset{OH}{C}}{-}\underset{OH}{\overset{H}{C}}{-}CH_3}$$

Crotonic acid (m. p. 72°) *dl-threo*-1,2-Dihydroxybutyric acid (m. p. 74–75°)

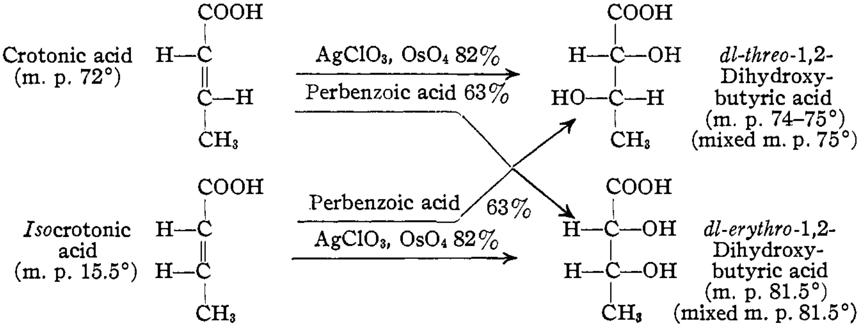
and



$$\mathrm{HOOC{-}\underset{H}{C}{=}\underset{H}{C}{-}CH_3} \xrightarrow[cis\ \mathrm{addition}]{\mathrm{AgClO_3,\ OsO_4}} \mathrm{HOOC{-}\underset{H}{\overset{OH}{C}}{-}\underset{H}{\overset{OH}{C}}{-}CH_3}$$

*Iso*crotonic acid (m. p. 15.5°) *dl-erythro*-1,2-Dihydroxybutyric acid (m. p. 81.5°)

These results are in perfect harmony with those obtained in the perbenzoic acid oxidations, which makes the configurations assigned to the



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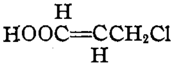
[23] By 100% in yield is meant that the isomer indicated was formed exclusively with very high yield. (For instance, in the oxidation of maleic anhydride with barium chlorate there was obtained exclusively mesotartaric acid with an actual yield of 91% and no trace of racemic tartaric acid.)

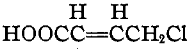
dihydroxybutyric acids above still more probable. A complete summary of all the oxidations carried out with chlorates and perbenzoic acid is given above.

A better means of determining these configurations would be the oxidation of the two acids to the corresponding tartaric acids, but this unfortunately appears to be impossible. There does, however, seem to be a possibility of obtaining better evidence by an indirect method. If the two 3-chloro acids[24] were prepared, their relation to crotonic and *iso*crotonic acids could be demonstrated by reduction with sodium amalgam. The oxidation of these chloro acids should yield a *threo* and an *erythro* 3-chlorodihydroxybutyric acid. Hydrolysis of these two acids should yield threonic and erythronic acids; oxidation should give mesotartaric and racemic acids; reduction should yield the two dihydroxybutyric acids. Work on these reactions is now in progress.

3-Chloro-crotonic acid



$HOO\overset{H}{C}{=}\underset{H}{C}CH_2Cl$



$HOOC\overset{H}{C}{=}\overset{H}{C}CH_2Cl$

3-Chloro-*iso*crotonic acid

Experimental Part

Materials

Crotonic Acid.—The commercial product may be used without further purification. The best method for its preparation has been recently described by Auwers.[25]

Isocrotonic Acid.—This was prepared from the commercial product and from Geuther's crude *iso*crotonic acid according to the method of Wislicenus.[26]

Lactone of 3-Hydroxy-isocrotonic Acid.—The lactone is a by-product in the preparation of *dl*-2,3-dihydroxybutyric acid and may be prepared according to Glattfeld's method[18] with good yield. The crude product was recrystallized twice from one and a half parts of absolute ether, cooled in ice and salt, and the crystals were dried at 0° over phosphoric anhydride in a vacuum desiccator. The melting point of the product was 5.0 to 5.3° (thermometer in the substance).

Perbenzoic Acid.—This was prepared according to Baeyer and Villiger,[27] except that chloroform was used instead of ether as a more suitable solvent for the benzoyl-peroxide. One has to be very sure that all of the materials used in the preparation of the peracid are pure because the oxidations require a long time and an impure peracid decomposes before the oxidations are complete.

Silver Chlorate.—The best method for the preparation of this substance consists in the solution of silver oxide in a slight excess of 10% chloric acid[28] at 30°. The filtrate is concentrated at reduced pressure and the concentrated solution of silver chlorate cooled in ice. The chlorate of silver is just as stable a compound as the chlorates of alkali metals.

The precipitate obtained in the silver chlorate oxidations is almost pure silver

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[24] The *trans* compound is known; Lespieau, *Bull. soc. chim.*, [3] **33**, 466 (1905); Auwers and Wissebach, *Ber.*, **56**, 732 (1923).

[25] Auwers, *Ann.*, **432**, 46 (1923).

[26] Wislicenus; see Beilstein's "Handbuch der organische Chemie."

[27] Baeyer and Villiger, *Ber.*, **33**, 1575 (1900).

[28] Vauquelin, *Ann. Chim.*, **95**, 124 (1915).

chloride. In order to purify it one has to wash it with warm dilute hydrochloric acid and then with water so as to remove oxalic acid and other impurities. It is dried as completely as possible by suction filtration. The pure, moist silver chloride thus obtained (containing about 6–8% of moisture) is suspended in five times its weight of water and, while the mixture is being violently stirred, a 50% excess of zinc dust is rapidly added. The solution becomes hot; the stirring is continued until the solution has cooled to room temperature and then the excess of the zinc is dissolved with 20% sulfuric acid without interrupting the stirring. The gray-brown precipitate is separated by filtration and washed thoroughly. The precipitate still contains a considerable amount of silver chloride and the operation must be repeated with a small amount of zinc dust in order to obtain pure silver, which may be used in the making of silver chlorate. The yields are almost quantitative.

Control of the Oxidations

The best control of the oxidations is the quantitative determination of the unsaturated compounds in the reaction mixture. No general method for this purpose has been published in the literature, as the behavior of unsaturated compounds differs very widely according to the reagents used in the determinations. Bromine water seems to be the most suitable reagent. When this reagent is used the acidity of the reaction mixture is very important; one group of unsaturated compounds—those having *active* double bonds—may be brominated quantitatively even in the presence of mineral acids, while another group—those having *inactive* double bonds—can be brominated only in neutral solution.

In order to find a reliable method for the control of the oxidations, many experiments were carried out for the determination of double bonds of unsaturated acids.

In every case a stock solution was made of such concentration that 25 cc. contained about 0.1 g. of unsaturated substance. In using Winkler's method,[29] there was added to 25 cc. of the stock solution 2 g. of potassium bromide, then 20 cc. of 10% sulfuric acid and 50 cc. of 0.1 *N* potassium bromate solution of known titer (organic solvent was not used). After two hours' standing in the dark the excess of bromine was measured iodimetrically. When the determinations were made with saturated bromine water, the procedure was as follows: 25 cc. of the stock solution was used

Table II

Results of Determinations

Acid	Calculated iodine number	Found with Winkler's method	Free acid	Found with satd. bromine water	
				Potassium acid salt	Neutral salt
Crotonic	295	297	...	...	...
*Iso*crotonic	295	297	...	...	...
Fumaric	218.8	7	106	193	216.7
Maleic	218.8	23	178	200	217.2
Lactone of 3-hydroxy-*iso*crotonic	302	trace	trace	...	187.0

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[29] See Meyer, "Analyse und Konstitutionsermittlung organischer Verbindungen," **1922.**

either as such (free acid) or after neutralization with 0.1 *N* alkali (without indicator). To this was added 10 cc. of saturated bromine water of known titer, the solution was left to stand for two hours in the dark and the excess bromine then titrated (Table II).

The lactone of the 3-hydroxy-*iso*crotonic acid has a very inactive double bond; it seems to be a heterocyclic compound. It suffers a complicated rearrangement with alkali and has maximum ability to absorb bromine only immediately after saponification.

As a result of this preliminary study the following procedures for the control of oxidations of the acids listed above were adopted.

In the oxidation of fumaric and maleic acids two samples are taken out from time to time: one is neutralized in the presence of indicator for the determination of the acidity and the other is titrated with bromine water after it has been neutralized without using indicator.

In the oxidation of the 3-hydroxy-*iso*crotonic lactone a sample is taken and heated with an excess of 0.1 *N* alkali for five minutes on the water-bath; after the solution has been cooled, the excess of alkali is titrated with 0.1 *N* sulfuric acid, using a very small amount of phenolphthalein, and the solution is then titrated immediately with bromine water.

In the oxidation of crotonic and *iso*crotonic acids the samples are titrated with alkali for the acidity and with bromine water without neutralization.

If there is silver in the solution, it must be precipitated with sodium chloride solution before testing.

The presence of osmic acid in the bromine titrations does not give any trouble as it does not oxidize hydrogen bromide in weakly acid solutions.

In the perbenzoic acid oxidations the amount of the peracid is measured iodimetrically. If it is necessary to titrate with bromine water, the samples are very much (at least ten times) diluted, as the peracid quickly oxidizes hydrobromic acid.

Oxidation of Crotonic Acid with Perbenzoic Acid

(a) **Oxidation in Chloroform Solution.**—Ten g. of crotonic acid was dissolved in 500 cc. of water, and 84 cc. of chloroform which contained 24 g. of perbenzoic acid (50% excess) was added. The mixture was shaken at room temperature in the dark.

Time	Start	2 weeks	4 weeks	5 weeks
$CHCl_3$ soln., cc.	0.2	0.2	0.2	0.2
0.1 *N* $Na_2S_2O_3$ soln., cc.	6.95	4.40	2.80	2.40

Both aqueous and chloroform solutions now required a negligible amount of bromine water.

The chloroform layer was then separated from the aqueous layer and the former was washed with 100 cc. of water. The united aqueous solutions were concentrated at reduced pressure to 300 cc., extracted three times with 50 cc. of chloroform and the water completely removed by further distillation. The residue was dried at a temperature of 40° and a pressure of 2 mm. for several hours. The pale yellow, viscous sirup weighed 12.2 g. (88% of the theoretical). The sirup was dissolved in 14 cc. of ethyl acetate and cooled to 0°. Crystallization took place as soon as the glass wall was scratched and the solution was transformed into a white semi-crystalline mass. After six hours' standing in ice, the mass was subjected to suction filtration and the crystals washed with cold ethyl acetate and dried at 40°, finally in a vacuum desiccator over phosphorus pentoxide. A yield of 8.65 g. of white crystals (m. p. 80.5°) was obtained.

From the mother liquor there was obtained 0.2 g. more of pure crystals, making a total yield of 8.85 g. or 63.5% of the theoretical.

The crystals were dissolved in 15 cc. of hot ethyl acetate, the solution treated with bone black and filtered hot by suction. The filtrate deposited as it cooled 7.4 g. of white crystals (m. p. 81.5°). A mixture of this acid with the acid obtained by the oxidation of *iso*crotonic acid with silver chlorate showed no depression of the melting point.

Titration. Subs., 0.3141, 0.3011: 25.85, 24.93 cc. of 0.1 *N* alkali (phenolphthalein). Calcd. mol. wt. for $C_4H_8O_4$: 120.06. Found: 121.5, 120.7.

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

(b) Oxidation in Aqueous Solution.—Ten g. of crotonic acid was dissolved in 500 cc. of water which contained 4 g. of perbenzoic acid. The solution was allowed to stand at room temperature. During the course of two months a total of 20 g. of crystallized peracid was added from time to time, and after six weeks 100 cc. of ether. Even after two months there was still present about 20% of the crotonic acid. The oxidation was interrupted and the reaction mixture worked up as before. The yield was 8.5 g. of sirup, which gave 5.5 g. of crystals (m. p. 80.5°) in two crops, 40% of the theoretical.

Oxidation of Isocrotonic Acid with Perbenzoic Acid

(a) Oxidation in Chloroform Solution.—Ten g. of pure, crystallizable *iso*crotonic acid (m. p. 15.5°) was dissolved in 200 cc. of water and 125 cc. of chloroform which contained 30 g. of perbenzoic acid was added. The mixture was shaken at room temperature in the dark.

After three weeks both aqueous and chloroform solutions required only a negligible amount of bromine water.

The reaction mixture was worked up in exactly the same manner as described above under the oxidation of crotonic acid. Thirteen g. of pale yellow sirup was obtained; 93% of the theoretical. This gave in two crops 8.75 g. of crystals (m. p. 73.5–74°) or 62.5% of the theoretical.

The crystals were recrystallized from hot ethyl acetate; 7.5 g. of crystals (m. p. 74–74.5°) was obtained. A mixture of this acid with the acid obtained by the oxidation of the crotonic acid with chlorates showed no depression of the melting point. The solubility of the product is almost the same as that of the acid of m. p. 81.5°.

(b) Oxidation in Water Solution.—Three and a half g. of *iso*crotonic acid (m. p. 15.0°) was dissolved in 175 cc. of water which contained 1.5 g. of perbenzoic acid. The solution was allowed to stand at room temperature. During the course of three months a total of 10.5 g. of peracid was added from time to time. After six weeks 50 cc. of ether was added. The yield was 4.0 g. of sirup which gave 3.22 g. of crystals (m. p. 73.5–74°) in two crops, or 65% of the theoretical.

Oxidation of Crotonic Acid with Chlorates. I. Barium Chlorate Oxidations

(A) Addition of Total Quantity of Chlorate in One Operation.—Twenty g. of crotonic acid was dissolved in one liter of water which contained 15.6 g. of barium chlorate (25% excess) and 2.5 cc. of a 1% solution of osmic acid. The solution was kept at room temperature in the dark.

Time	Start	2 days	4 days	6 days
Solution, cc.	2	2	2	2
0.1 *N* alkali, cc.	4.65	4.30	3.75	3.50
Satd. bromine water, cc.	3.2	2.3	1.1	0.2

No pressure developed in the bottle. The solution was then separated by filtration from a small amount of crystals, which proved to be barium oxalate.

Anal. Subs., 0.3276: loss in weight at 150–160°, 0.0444; $BaSO_4$, 0.2917. Calcd. for $C_2O_4Ba\cdot 2H_2O$: H_2O, 13.78; Ba, 52.54. Found: H_2O, 13.56; Ba, 52.40.

The filtrate from the barium oxalate was extracted twice with 200 cc. of benzene; the water solution was then concentrated to a thin sirup at reduced pressure. The sirup was dissolved in one liter of water and the solution again subjected to distillation in order to remove all of the volatile acids. The residue of the second distillation was dissolved in 300 cc. of water and the excess of barium chlorate was reduced with sulfur dioxide gas. The barium sulfate was separated by filtration and the filtrate concentrated to two-thirds of its volume at reduced pressure. Then the sulfuric and hydrochloric acids were completely removed with barium hydroxide and silver oxide.

The purified solution, which contained the dihydroxybutyric acid and about 20% of the crotonic acid as chlorohydroxybutyric acid, was evaporated to a thick sirup and finally dried at a temperature of 40° and a pressure of 10 mm. for several hours. The yield was 22 g. of pale yellow sirup. This was dissolved in 20 cc. of absolute ethyl acetate and the solution cooled in ice. Crystallization began as soon as the glass walls were scratched. After twelve hours' standing in ice the crystals were separated by filtration, washed carefully with cold ethyl acetate and dried at 40°: Crop I, 8.4 g. of white crystals (m. p. 73.5°); Crop II (see later), 2.0 g. of white crystals (m. p. 72.5°); total, 10.4 g. of white crystals (m. p. 73°), or 38% of the theoretical.

These crystals were recrystallized from hot ethyl acetate and 9.0 g. of crystals (m. p. 74–74.5°) was obtained.

Titration. Subs., 0.2945, 0.3845: 24.31, 31.70 cc. of 0.1 *N* alkali. Calcd. mol. wt. for $C_4H_8O_4$: 120.06. Found: 121.1, 121.3.

The mother liquor from Crop I was diluted with ethyl acetate to 50 cc. and was shaken once with 50 cc. of water. The two solutions were treated separately.

(a) Water Solution.—The solution was evaporated at reduced pressure and the residue dried and crystallized from ethyl acetate in the usual manner. Two g. of crystals (m. p. 72.5°) was obtained (Crop II). They were united with Crop I.

(b) Ethyl Acetate Solution.—This was shaken twice with 20 cc. of water and the ethyl acetate layer dried with sodium sulfate, evaporated and the residue dried at 70° for several hours at reduced pressure. The yield was 1.75 g. of sirup, which did not crystallize. A sample of 0.1745 g. required 12.24 cc. of 0.1 *N* alkali and after saponification with 0.1 *N* alkali 11.47 cc. of 0.1 *N* silver nitrate; calcd. for chlorohydroxybutyric acid, $C_4H_7O_3Cl$: mol. wt., 138.5; Cl, 25.6. Found: mol. wt., 142; chlorine, 23.3.

About 20 g. of this crude chlorohydroxybutyric acid obtained from different experiments was dissolved in 50 cc. of water and the solution extracted twice with 150 cc. of ether. The residue obtained from the ethereal solution was dissolved in 50 cc. of water and the solution neutralized with zinc carbonate. The concentrated solution of the zinc salt deposited 2.0 g. of crystals after standing for three days in ice. A sample of 1.8 g. of the crystallized zinc salt was dissolved in 30 cc. of water, 20 cc. of 10% sulfuric acid was added and the solution extracted with ether, etc. The residue of the ether solution weighed 1.1 g. This was dissolved in 1 cc. of ether and crystallized in ice: 0.3 g. of white crystals (m. p. 76°) was obtained.

Anal. Subs., 0.0991: 6.98 cc. of 0.1 *N* alkali for free acid; 7.18 cc. of 0.1 *N* alkali and 7.22 cc. of 0.1 *N* silver nitrate for organically bound chlorine after saponification on the water-bath for fifteen minutes. Calcd. for $C_4H_7O_3Cl$: mol. wt., 138.5; Cl, 25.6. Found: mol. wt., 142; Cl, 25.8.

(B) **Gradual Addition of Chlorate During Oxidation.**—Twenty g. of crotonic acid was dissolved in one liter of water which contained 5 cc. of a 1% osmic acid solution.

Then in the course of three weeks 15.6 g. of barium chlorate was added in about 0.4-g. lots whenever the solution became brown. After four weeks the crotonic acid had entirely disappeared. The decrease in the initial acidity was about 24%. The reaction mixture was worked up as before. The yield of the oxidized product was 24.9 g. and that of the dihydroxybutyric acid (m. p. 72°) 13.5 g. or 48% of the theoretical. The amount of the chlorinated compound was a little less than under (A).

II. Oxidation with Potassium Chlorate

Twenty g. of crotonic acid was dissolved in one liter of water which contained 5 cc. of a 1% solution of osmic acid. Then in the course of three weeks 12 g. of potassium chlorate was added in about 0.3-g. lots whenever the solution became brown. After four weeks the oxidation was complete. There was a 24% decrease in the acidity. The solution was extracted with benzene and the excess of potassium chlorate was reduced with sulfur dioxide gas in the usual manner. The sulfuric acid was precipitated with barium hydroxide; the potassium chloride remained in solution. The residue from the distillation of the water solution was dissolved in 20 cc. of absolute alcohol and absolute ethyl acetate was added until no more precipitation occurred (about 600 cc. of ethyl acetate).

(a) Precipitate.—This was treated with 150 cc. of hot absolute alcohol and the potassium chloride removed by filtration in the hot. The filtrate contained only a trace of chlorine and deposited on cooling 10.9 g. of white crystals (m. p. about 104–106°, not sharp). The product was easily soluble in hot absolute alcohol, from which it may be recrystallized; it is insoluble in ethyl acetate.

Anal. Subs., 0.5121: 17.0 cc. of 0.1 *N* alkali; $KClO_4$, 0.2537. Calcd. for $C_4H_7O_4K \cdot C_4H_8O_4$: acid, 43.3; K, 14.05. Found: acid, 40.0; K, 13.98.

Three g. of the double salt was dissolved in 400 cc. of water and 11 cc. of *N* sulfuric acid was added. The solution was then distilled to dryness at reduced pressure, the residue was dissolved in ethyl acetate, etc., in the usual manner. Two and six-tenths g. of a crystalline mass was obtained which yielded 2.0 g. of crystals (m. p. 74°) in two crops.

(b) Ethyl Acetate Solution.—The residue obtained by the removal of the ethyl acetate at reduced pressure weighed 14.8 g., which gave 3.2 g. of crystals (m. p. 73°) from ethyl acetate. The mother liquor of the crystals contained about 20% of the crotonic acid as chlorohydroxybutyric acid.

III. Oxidation of Crotonic Acid with Silver Chlorate

(A) Silver Chlorate in Excess.—Twenty g. of crotonic acid was dissolved in one liter of water which contained 18.3 g. of silver chlorate and 2.5 cc. of a 1% solution of osmic acid. The reaction mixture stood at room temperature. The precipitation of the silver chloride began immediately and the solution turned milky.

After 5 days a sample required only a negligible amount of bromine water. At the end of the oxidation there was a slight pressure in the flask. The silver chloride was separated by filtration. According to analysis it contained a small amount of silver oxalate.

The filtrate from the silver chloride was extracted with benzene and evaporated at reduced pressure. A large amount of crystals appeared. These were dissolved in water and the distillation was repeated. The residue was treated with 100 cc. of absolute alcohol and the crystals were separated by filtration.

(a) Crystals.—These proved to be the silver salt of the dihydroxybutyric acid (m. p. 74°); weight, 4.5 g.

Anal. Subs., 0.9420, 0.4905: 41.40, 21.62 cc. of 0.1 *N* KCNS. Calcd. for $C_4H_7O_4Ag$: Ag, 47.54. Found: Ag, 47.4, 47.56.

Eight g. of this salt from different experiments was dissolved in water and the calculated amount of hydrochloric acid was added, etc.; yield, 4.0 g. of sirup, which gave 3.1 g. of crystals (m. p. 74°).

(b) Alcoholic Solution.—This was evaporated at reduced pressure, the residue treated with ethyl acetate, the solution filtered and the filtrate distilled to dryness. The pale yellow sirup which remained weighed 23 g. and gave 12.8 g. of crystals (m. p. 74°) in two crops from ethyl acetate; total yield (acid and silver salt) was 54% of the theoretical. The mother liquor of the crystals contained about 5% of the crotonic acid as chlorohydroxybutyric acid.

In other cases, when the silver salt was not separated and the oxidation lasted for about two weeks and somewhat more silver chlorate was used (20 g. of silver chlorate for 20 g. of crotonic acid), the yields of dihydroxybutyric acid (m. p. 74°) averaged 60% of the theoretical.

(B) Oxidation by Gradual Addition of Silver Chlorate.—Twenty g. of crotonic acid was dissolved in one liter of *ice water* which contained 10 cc. of a 1% osmic acid solution and little by little 18.0 g. of crystallized silver chlorate was added in about four weeks, while the solution was kept in *ice water.* The oxidation was rapid at the beginning; 0.5 g. of chlorate was added as a first portion; the solution became milky within a few minutes and turned brown in three hours. Then on every succeeding day for about two weeks, one g. of chlorate was added in 0.5-g. portions; the oxidation then became slower and 0.5 g. of chlorate was added whenever the solution turned yellow. Finally, the reaction mixture was removed from the ice-bath and allowed to stand at room temperature for a few days. After 18.0 g. of chlorate had been added, the solution remained colorless, showing that no more oxidizable substance was present.

There was no change in the initial acidity and no trace of crotonic acid, but a trace of chlorinated compound was found. The silver precipitate was separated by filtration and washed with dilute hydrochloric acid, giving 13.15 g. of silver chloride. A very small amount of oxalic acid was separated from the hydrochloric acid filtrate.

The filtrate from the silver chloride was distilled at reduced pressure, the excess of silver chlorate (about 0.5 g.) was reduced with sulfur dioxide gas, etc., in the usual manner. The residue from the water solution was a colorless, very viscous sirup which weighed 26.7 g.; 96% of the theoretical. The yield from ethyl acetate in three crops was 23.05 g. of crystals (m. p. 74°) or 82.5% of the theoretical.

The crystals were recrystallized from 40 cc. of ethyl acetate and yielded in two crops a total of 20.8 g. of crystals (m. p. 74.5–75°).

The non-crystallizable residue of the crude crystals weighed 2.7 g.

When the oxidation was carried out at room temperature in the manner described above and when half the amount of osmic acid was used, the yield was 92% of sirup and 70% of the dihydroxybutyric acid (m. p. 74°).

Oxidation of Isocrotonic Acid by Gradual Addition of Silver Chlorate

Six g. of pure *iso*crotonic acid (m. p. 15.0°) was dissolved in 300 cc. of *ice water* which contained 2.5 cc. of a 1% osmic acid solution. Then in four weeks 53 cc. of a 10% silver chlorate solution was added in 1.5-cc. portions while the solution was kept in an *ice-bath* in the dark, etc., as described in the silver chlorate oxidation of crotonic acid under (B). There was no change in the acidity and only a trace of chlorinated compound was found. The yield was 8.05 g. of colorless sirup or 96% of the theoretical. The sirup gave from ethyl acetate in two crops 6.88 g. of crystals (m. p. 81°) or 82%

of the theoretical. The product was recrystallized from 20 cc. of ethyl acetate; 6.0 g. of crystals (m. p. 81.5°) was obtained.

Oxidation of the Lactone of 3-Hydroxy-isocrotonic Acid with Silver and Barium Chlorates

(A) Silver Chlorate.—Ten g. of the lactone (m. p. 5.0°) was dissolved in 100 cc. of water which contained 5 cc. of a 1% osmic acid solution, and ten g. of silver chlorate was added in the course of two months. The reaction mixture stood at room temperature. In the first three additions 2 g. of chlorate was added; thereafter 0.5 g. of chlorate whenever the solution turned brown. At the end of the oxidation there was a slight pressure in the bottle. The titration showed that about 60% of free acid and 40% of lactone was present.

The silver chloride was separated by filtration (the silver precipitate did not contain any oxalate), the filtrate diluted to 250 cc., extracted with benzene, distilled at reduced pressure to a thick sirup and finally the residue was dried at a temperature of 50° and a pressure of 2 mm. for several hours. The sirup contained only a trace of organically bound chlorine.

This sirup (13.3 g.) was dissolved in 15 cc. of absolute acetone and the solution cooled in ice. During six hours the solution deposited 7.1 g. of crystals (m. p. 89–90°).

The mother liquor was concentrated to a thick sirup, which was dried at a pressure of 2 mm. and a temperature of 70° for two hours. The residue gave 2.2 g. of crystals from absolute acetone. A third crystallization in the same way yielded 1.0 g. of crystals.

The final mother liquor was subjected to distillation at a temperature of 130–150° and a pressure of 1 mm. but suffered partial decomposition. The distillate gave 0.2 g. of crystals from absolute acetone. The total yield of crystallized product was 10.5 g. or 75% of the theoretical.

The crystals were dissolved in 100 cc. of hot absolute acetone, the solution was subjected to filtration in the hot and the filtrate concentrated to 30 cc. This solution deposited after ten hours' standing in ice 8.0 g. of crystals (m. p. 92°).

Two g. of crystals (m. p. 92°) was dissolved in 10 cc. of dilute nitric acid (sp. gr., 1.22) and the solution was kept at 60° for forty-five hours, that is, until evolution of brown fumes had ceased. The nitric acid was removed by distillation at reduced pressure in the usual manner. The crystalline residue was dissolved in 300 cc. of water, the solution neutralized with alkali, heated to boiling and a small amount of calcium acetate solution added until no more precipitation occurred. After ten minutes the calcium oxalate was removed by filtration in the hot. The calcium oxalate was dissolved in dilute hydrochloric acid and again precipitated in the usual manner. The precipitate was washed with hot water and then dried at 105° to constant weight; 0.34 g. of substance was obtained.

Anal. Subs. 0.3393: CaO, 0.1294. Calcd. for $CaC_2O_4 \cdot H_2O$: CaO, 38.34. Found: CaO, 38.14.

The filtrate of the calcium oxalate was acidified with dilute hydrochloric acid and concentrated to 75 cc. at reduced pressure. Then the solution was heated, neutralized and the calcium mesotartrate precipitated with an excess of calcium acetate. After twenty-four hours the precipitate was separated by filtration, washed with warm water and dried in the air for eighteen hours. Three g. of air-dried calcium salt was obtained.

Anal. Subs., 0.2329: loss in weight at 180°, 0.0521; ash, 0.0538. Calcd. for $C_4H_4O_6Ca \cdot 3H_2O$: H_2O, 22.32. Found: 22.37. Calcd. for $C_4H_4O_6Ca$: CaO, 29.81. Found: CaO, 29.76.

This shows that the oxidation yielded, except for a small quantity of oxalic acid, exclusively mesotartaric acid.

(B) **Barium Chlorate.**—Ten g. of lactone (m. p. 5.0°) was dissolved in 100 cc. of water which contained 5 cc. of a 1% solution of osmic acid and 9.2 g. of barium chlorate was added during two months, etc., in just the same manner as described under (A). The yield was 12.7 g. of sirup, which gave 9.1 g. of crystals (m. p. 90°), or 64% of the theoretical. There was found only a trace of organically bound chlorine.

Oxidation of Maleic Anhydride with Barium and Silver Chlorates

(A) **Barium Chlorate.**—Ten g. of maleic anhydride (m. p. 54°) was dissolved in 500 cc. of water which contained 12.0 g. of barium chlorate and 2.5 cc. of a 1% osmic acid solution. The mixture stood at room temperature. At the beginning the solution became yellow; the color later disappeared. The oxidation was complete in two months; the solution required only a negligible amount of bromine water. There was no change in acidity.

The solution was then extracted with benzene, the excess of barium chlorate reduced with sulfur dioxide gas and the sulfuric and hydrochloric acids were removed in the usual manner. The purified water solution was evaporated at reduced pressure and the crystallized residue dried at a temperature of 40° and a pressure of 8 mm. for three hours. The yield was 15.0 g. of white crystals which contained, according to titration, 13.9 g. of mesotartaric acid or 91% of the theoretical.

The water solution of the acid did not give a precipitate with calcium sulfate water, showing the absence of racemic tartaric acid. The product did not contain a trace of chlorine and required only a trace of bromine water after neutralization.

The oxidation of the maleic anhydride therefore gave exclusively mesotartaric acid.

(B) **Silver Chlorate.**—Ten g. of maleic anhydride was dissolved in 500 cc. of water which contained 12.0 g. of silver chlorate and 2.5 cc. of a 1% solution of osmic acid. The oxidation was complete in two months, the solution requiring a negligible amount of bromine water. There was a 26% decrease in the acidity. The reaction mixture was worked up as described under (A). The pure solution of the oxidized product did not give a precipitate with calcium sulfate water and contained, according to titration, 10.3 g. of mesotartaric acid or 67% of the theoretical.

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Summary

1. The oxidation of crotonic and *iso*crotonic acids with perbenzoic acid is described. Crotonic acid gave a *dl*-1,2-dihydroxybutyric acid (m. p. 81.5°) with a yield of 63.5% of the theoretical. *Iso*crotonic acid gave a *dl*-1,2-dihydroxybutyric acid (m. p. 74–75°) with a yield of 62.5%.

2. The oxidation of crotonic and *iso*crotonic acids with silver chlorate in the presence of osmic acid as a catalyst was carried out. Crotonic acid gave a *dl*-1,2-dihydroxybutyric acid (m. p. 74–75°) with a yield of 82.5%. Isocrotonic acid gave a *dl*-1,2-dihydroxybutyric acid (m. p. 81.5°) with a yield of 82.5%.

3. A study of the results of the oxidation of crotonic acid with various chlorates in the presence of osmic acid is described. It was shown that in the chlorate oxidations the reduction of chlorates proceeds through the lower oxides of chlorine and the mechanism of these oxidations is discussed.

4. The most probable structure of the two theoretically possible *dl*-1,2-dihydroxybutyric acids is suggested.
5. A modified procedure for the oxidation of the lactone of 3-hydroxy-*iso*crotonic acid with silver and barium chlorates is given.
6. The results of a comparative study of the oxidation of maleic anhydride with silver and barium chlorates are given.

CHICAGO, ILLINOIS

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ELECTRON DISPLACEMENT IN CARBON COMPOUNDS. V. THE ADDITION OF HYDROGEN CHLORIDE TO 3-ETHYL-2-PENTENE[1]

BY HOWARD J. LUCAS

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In order to account for the products formed when strong acids add to derivatives of ethylene, investigators have proposed different hypotheses. Markownikoff[2] many years ago laid down the rule that when hydrogen bromide or other similar compound adds, the negative atom goes to that unsaturated carbon atom which is joined to the larger number of other carbon atoms. But there are many exceptions to this rule, the best recognized being acrylic acid, which with hydrogen bromide forms β-bromo-acrylic acid instead of α-bromo-acrylic acid.

An extension of the Lewis theory of molecular structure[3,4] offers another explanation for these phenomena based upon the electron attraction of radicals.

Making use of the formula diagrams, it is evident that a comparison of these values for H, CH_3 and C_2H_5 is all that need be considered. If the usually accepted order of electron attraction, *viz.*, $H > CH_3 > C_2H_5$, is correct,[4] then carbon atom C—2 must have a stronger attraction for the four electrons of the double bond than C—3, since its other four electrons are attracted more strongly by H and CH_3 than are the other four electrons about C—3.[5] Thus C—2 is negative with respect to C—3 (b) and when

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[1] Presented at the Claremont meeting of the Pacific Section, American Association for the Advancement of Science, June 15, 1928.

[2] Markownikoff, *J. prakt. Chem.*, **48**, 345, 452 (1892).

[3] Lewis, THIS JOURNAL, **38**, 762 (1916).

[4] Lucas and Moyse, *ibid.*, **47**, 1459 (1925); Lucas, *ibid.*, **48**, 1827 (1926). See also Kharasch and Grafflin, *ibid.*, **47**, 1948 (1925); Kharasch and Marker, *ibid.*, **48**, 3130 (1926).

[5] From their work on the polarization of the isomeric heptanes, Smyth and Stoops, THIS JOURNAL, **50**, 1889 (1928), conclude that any electron shifts existing in these hydrocarbons are so small that they have no appreciable effect upon properties. They also maintain that these and other results provide strong evidence against the assumption