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

# HALOGENATION OF FUMARIC AND MALEIC ACIDS. A NOTE ON THE WALDEN INVERSION[1]

By Ethel M. Terry and Lillian Eichelberger

Students of valence have long been interested in the fact that the addition of bromine to fumaric[2] or maleic acid[3] has resulted in dibromo acids of configuration which does not correspond to that of the acids from which they were made. According to Wislicenus'[4] deduction from the Le Bel-van't Hoff theory, it would be anticipated that the bromine atoms would attach themselves in place of one of the two bonds between the alpha and beta carbon atoms, thus forming a so-called *cis* addition product. From maleic acid (or its anhydride), there should result dibromo-succinic acid, the *meso* form, and from fumaric acid there should result *iso*dibromo succinic acid, the racemic form. Actually, however, the main product of the bromination of maleic acid is the racemic acid, and of fumaric acid is the *meso* form. The corresponding isomers result also from chlorination. They are called *trans* addition products.

The situation has been especially mystifying, since when fumaric and maleic acids are oxidized in neutral solution to tartaric acid by potassium permanganate,[5] the acids produced are exactly those demanded by the theory, namely, *meso*tartaric acid from maleic acid, and racemic acid from fumaric acid.

As has been pointed out by others, the most striking difference in the halogenation experiments on the one hand, and the permanganate oxidation on the other, is that in the first the acids are used, whereas in the second their neutral salts undergo change. The present report gives the result of causing the addition of halogen to the latter compounds in water solution, so that there are now available the results of halogenation both of fumaric and maleic acids, and of their respective salts.

The necessary condition for the success of the experiments was that we suppress the hypohalous acid formation which normally occurs when bromine or chlorine is passed into neutral water solution. This was accomplished by the addition to the reaction mixture of an excess of neu-

[1] The material of this paper was presented to the Organic Division of the American Chemical Society at its April meeting of 1924, at Washington, D. C.

[2] (a) Baeyer, *Ber.*, **18**, 676 (1885). (b) Kirchhoff, *Ann.*, **280**, 209 (1894). (c) Kékulé, *Ann. Spl.*, **1**, 131 (1860). (d) Fittig and Petri, *Ann.*, **195**, 56 (1879).

[3] (a) McKenzie, *J. Chem. Soc.*, **101**, 1200 (1894). (b) Ref. 2 b, p. 207. (c) Michael, *J. prakt. Chem.*, [2] **52**, 293 (1895). (d) Ref. 2 d, pp. 58, 60. (e) Kékulé, *Ann. Spl.*, **2**, 87 (1861). (f) Pictet, *Ber.*, **13**, 1670 (1880).

[4] Wislicenus, *Abhdlgn. d. sächs. Geselsch. d. Wissensch.*, **14**, No. 1 (1887).

[5] Kekulé and Anschütz, *Ber.*, **13**, 2150 (1880); *Ann.*, **226**, 191 (1884). Tanatar, *Ber.*, **12**, 2293 (1879); *ibid.*, **13**, 1383 (1880).

tral bromide or chloride salt. The very high concentration of negative halogen ion $X^-$ furnished prevented the usual hydrolysis of halogen ($X_2$ + $H_2O$ = $X^-$ + HOX + $H^+$) from producing enough hypochlorous or hypobromous acid for it to take an appreciable part in the reaction. Without the excess of halide ion, the principal products of the halogenation of the neutral salts of maleic and fumaric acids are salts of the halogen malic acids (COOH—CHX—CHOH—COOH), but with the excess concentration of halogen ion present, dihalogen succinic acid (COOH—CHX—CHX—COOH) salts are produced.

Representative results of these experiments (all carried out at room temperature) are tabulated below. The column headings are self-explanatory. For the sake of later reference, the data of Anschütz on the permanganate oxidation, already spoken of, are included. The data are arranged in the order of the increasing weight of the group added.

TABLE I

REPRESENTATIVE RESULTS

| Substance and concentration Moles per liter | Groups added | Salt concn. $N$ | | Yield % | Proportion of yield which is cis addition product % |
|---|---|---|---|---|---|
| Sodium maleate | OH | .. | ... | .. | Chief product (meso) |
| Sodium fumarate | OH | .. | ... | .. | Chief product (racemic) |
| Sodium maleate 0.715 | Cl | NaCl | satd. | 66 | 100 (dichloro) |
| Sodium fumarate 0.681 | Cl | NaCl | satd. | 68 | 100 (isodichloro) |
| Sodium maleate 0.953 | Br | NaBr | 4.8 | 89 | 78 (dibromo) |
| Sodium fumarate 0.681 | Br | NaBr | 3.8 | 92 | 10 (isodibromo) |

It will be seen that when hydroxyl or chlorine is added, cis addition occurs virtually exclusively. When bromine is added, however, the situation is a little more complex. In this case, sodium maleate undergoes cis addition to the extent of 78% of the total yield, but sodium fumarate only to 10%. Not only sodium, but potassium and strontium salts were used in similar experiments, but the results were the same. In the case of sodium fumarate, a buffer solution was also employed in one experiment, but without change of result. In another experiment, the temperature of the reaction mixture was lowered to —2° but without effect. The concentration of bromine ion was varied considerably (the concentration of the sodium bromide varied from 1 to 7 $M$), but again the same results were obtained. Hence, we believe that the table gives truly representative results of the halogenation of the neutral salts of fumaric and maleic acids, respectively.

It should be pointed out that the neutral salts of the acids in question undergo halogenation at far greater speeds than do the acids themselves,

either in water or in non-ionizing solvents.[6]  It seems, therefore, certain that in the neutral-salt reaction, the ions (or the salt molecules) are the active units, whereas in solutions of the acids in non-ionizing media, at least, acid molecules are active.

Apparently the weight of the group added should be considered, since in the case of the addition of the relatively light hydroxyl or chlorine, *cis* addition succeeds admirably, but not in the case of bromine addition.  It is of interest that in the halogenation of maleic anhydride the weight of the added group is also a critical factor.  Holmberg[7] reports that the product of the chlorination of maleic anhydride dissolved in chloroform and the solution exposed to sunlight at ordinary temperatures consists of five parts of *trans* addition product (anhydride of the *iso*dichloro acid) to one part of *cis* addition product (anhydride of dichloro acid).  On the other hand, no *cis* addition of bromine occurs when maleic anhydride is brominated in chloroform solution exposed to sunlight[8] or in ether[9] solution without exposure to light (both reactions at ordinary temperature). Data on the halogenation of the maleic anhydride are to be preferred to those on the halogenation of the maleic acid, since in the case of the latter concomitant transmutation of the acid makes the interpretation of the results difficult.  We conclude that the weight of the added group is critical both in the halogenation of the acids and their salts.

The fact that *cis* addition is the principal reaction in the bromination of the neutral maleates but *trans* addition is the chief process in the bromination of the fumarates indicates some difference in work necessary to the two processes with the respective substances.  The dibromo acid is the more stable of the two dibromosuccinic acids, and is the one formed in large proportion in bromination of both of the salts in question.

**Summary of Observations.**—There are then three variables that affect the nature of the products: (a) the ions of the acids in question favor *cis* addition, but the molecules favor *trans* addition; (b) *cis* addition is favored the lighter the group added, and *trans* addition the heavier the group added; (c) as between *cis* and *trans* addition that which accomplishes the formation of the more stable isomer (the *meso* form) is the more favored.  The outcome of any given set of experimental conditions is the resultant of these

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[6] In the above discussion we are comparing the neutral salt with the non-ionized acid, and are not considering the acid salt.  The latter acts just as the theory to be presented would predict, namely, in water solution part *cis* and part *trans* products form in bromination.  Since the proof that the acid ion is the unit undergoing change involves elaborate experiments on the rates of reaction, we will present those data separately.  For the present it is sufficient to note that the acid ion furnishes no fundamentally new or conflicting results.

[7] Holmberg, *Svensk. Kem. Tids.*, **24**, 105 (1912).

[8] Ref. 3 c, pp. 292–293.

[9] McKenzie, *J. Chem. Soc.*, **101**, 1200 (1912).

influences. Any theory of the mechanism of the processes involved must take these three points into consideration.

**Older Theories.**—As has been stated, the main features of the problem of the behavior of the double bond have been recognized for some time. The difference in result of permanganate oxidation of the salts, and halogen addition to the acids has been ascribed by Michael to a difference in structure between acid and salt of maleic and fumaric acids, respectively.[10] However, it will be noticed that this simple theory cannot deal with the peculiar case of sodium fumarate. When this salt adds bromine, *trans* addition is the principal process, but when it adds chlorine, *cis* addition is followed.

Werner and Pfeiffer[11] have suggested that *cis* addition occurs in the permanganate oxidation of the sodium salts because an oxygen atom is picked up at the double bond and this prevents free rotation; thus, NaOOCCH—CHCOONa. The substance formed is then hy-

drolyzed and yields sodium tartrate. However, an acid of the structure of this compound, namely, fumaryl-glycidic acid has been found by Lossen.[12] It is quite stable, hydrolyzes slowly in water to form tartaric acid (with by-products) and forms soluble calcium salts. But in the reaction in question, the tartaric acid salts form at once as a result of the permanganate reaction. The blue copper tartrate complex can be made with the solution immediately upon filtration from the precipitated manganese dioxide. The calcium salts may also be precipitated. It seems, therefore, impossible that this fumaryl-glycidic acid can be the intermediate compound.

It has been suggested that bromine itself catalyzes the *trans* addition process just as it does the transmutation of maleic to fumaric acid. We note, however, that in the addition of bromine, sodium maleate can be made to form *cis* addition product nearly completely, but that sodium fumarate cannot. If the catalytic influence of bromine were critical, then the first and not the second should be the difficultly controllable reaction for bromine should cause *trans* addition in the former case if in any.
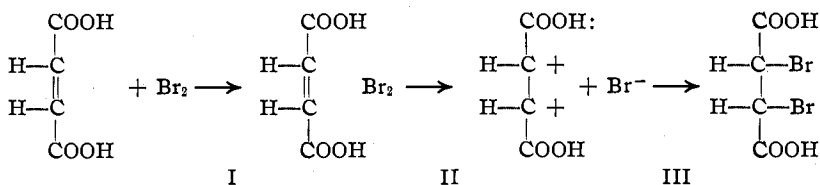
**A New Theory of the Oxidation of the Double Bond.**—A new theory of the mechanism of the processes under discussion will now be set forth.

Suppose that there is an association between maleic acid and halogen, and that an exchange of electrons occurs prior to primary valence-compound formation. After this change, union of oppositely charged ions should follow. These three stages are represented below.

[10] Michael, *Am. Chem. J.*, **39**, 14 (1908).
[11] Pfeiffer, *Z. physik. Chem.*, **48**, 40 (1904).
[12] Lossen, *Ann.*, **348**, 300 (1907).

$$
\begin{array}{ccccccc}
\underset{\substack{|\\ \text{H}-\text{C}\\ \|\\ \text{H}-\text{C}\\ |\\ \text{COOH}}}{\text{COOH}} + \text{Br}_2 \longrightarrow & \underset{\substack{|\\ \text{H}-\text{C}\\ \|\\ \text{H}-\text{C}\\ |\\ \text{COOH}}}{\text{COOH}} \; \text{Br}_2 \longrightarrow & \underset{\substack{|\\ \text{H}-\text{C}+\\ \\ \text{H}-\text{C}+\\ |\\ \text{COOH}}}{\text{COOH:}} + \text{Br}^- \longrightarrow & \underset{\substack{|\\ \text{H}-\text{C}-\text{Br}\\ \\ \text{H}-\text{C}-\text{Br}\\ |\\ \text{COOH}}}{\text{COOH}} \\
\text{I} & \text{II} & \text{III} &
\end{array}
$$

As an alternative assumption, we may consider that a discharge of electrons occurs between bromine and maleic acid without any preliminary association. Obviously, either route or both might be followed. However, if the second were the principal process of the reaction, chlorine should react more readily than bromine in the cases in question. But the opposite is true, as is frequently the case in reactions of halogens with the double bond. The conclusion, therefore, seems unavoidable that the fast halogenations begin with an association made possible by the so-called stray fields of the halogen molecule and the double bond. We have imagined that a certain amount of work was done upon two of the four electrons of the double bond so that they changed their positions and finally shifted to the positive bromine atom. As has been stated, a third stage, namely of union of ions, must follow, since up to this time no primary valence union has been possible.

Obviously, in the first stage of addition some special orientation of molecules with respect to each other may occur as directed by their magnetic fields. However, in the cases in hand, this question need not be considered.

In what follows, the hypothetical intermediate ion with the free positive charges on the alpha and beta carbon atoms will be called the intermediate ion.

In the development of our theory, we attempted to test the existence of this ion. If the third stage were slow relative to the rate of arrival of ions from surroundings, it should be possible, for example, to build a dichloride by the action of bromine and potassium chloride on sodium maleate. If such a reaction occurred, it could be definitely established, since all possible products are stable under the necessary conditions of the experiments. This attempt was made at length, and at first we thought that we had succeeded, but with a very careful review of our experimental methods, we were forced to admit that we had only chloride-bromide and not dichloride products. Similar experiments were carried out with fumaric acid and with ethylene as well as with maleic acid. Incidentally, we tried the action of potassium permanganate on sodium maleate in dilute aqueous solution in the presence of a large excess of potassium bromide under conditions with which a good yield of tartaric acid could be obtained. Tartaric acid was again formed, but only small traces of dibromo acid were found, such as might have been found by the reaction of minimal quantities of bromine liberated by the action of potassium permanganate on

potassium bromide. The third stage of the halogenation of the double bond, therefore, must occur at rates too fast for appreciable participation of ions from solution in the reaction. This conclusion is after all completely in harmony with our knowledge of chemical reaction. It would be strange, indeed, to find changes between charged atoms, distant from each other the diameter of a molecule, to go on at speeds comparable to the diffusions of ions in solution.

Returning now to the mechanism presented, the critical point of the theory is that it indicates the possible existence of a force which, if unchecked, should bring about a change in configuration of the original ethylene derivative during addition. For example, when first formed, the intermediate ion of maleic acid should have the structure shown in Fig. 1A.
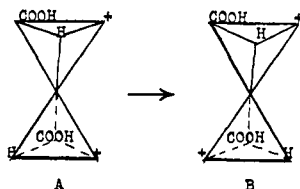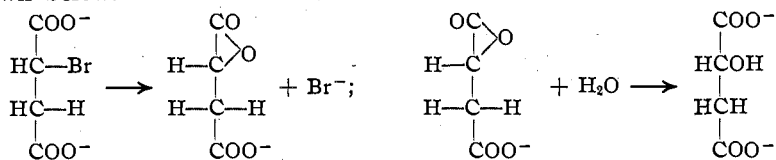


Fig. 1.

The repellent effect of the adjacent charges should be immediately felt. According to the conception of atomic structure now common, the net result of the repulsion should be a movement of hydrogen, the lighter of the two groups on one of the carbon atoms, to a position to cover the initial positive charge on that atom as shown in Fig. 1. This would occur, because of the stress put upon the two electrons between the hydrogen and the carbon. After this change, a positive charge would be found where the hydrogen had first been located, so that now the free charges would be at a maximum distance apart. This is shown in Fig. 1B. Union of negative ions with the new ion would give a product of opposite configuration to that of the initial acid, and it would be a so-called *trans* addition product. It will be noted that the mobile hydrogen need not change its distance from the carbon kernel during this movement. It is to be supposed that these changes are rapid relative to kinetic agitation which would obviously accomplish the same spreading of the charges without necessarily causing a change in configuration. That is, the carbon atoms might rotate about the alpha and beta carbon union without change of relative position of the attached groups. Such a change should, however, be relatively slow.

In the case of fumaric acid, a similar intermediate ion should form, and rearrangement follow in a similar way. Maleic anhydride and the esters of maleic and of fumaric acids would also form such ions and in bromination should undergo *trans* addition of bromine as is the fact.

In the case of the neutral salt ions, the negative charges on the neighboring carboxyl groups should reduce the tendency for rearrangement. Presumably carboxyl would be drawn to the positive charge and lactone formation could follow, provided a bromine ion did not reach the positive charge first. A similar lactone formation is definitely established in the case of hydrolysis of monobromosuccinic acid.[13] There it could be shown that bromine ion was liberated at a rate that was more rapid than the rise of acidity. The hydrolysis must then occur after lactone formation as shown below.

$$
\begin{array}{ccccccc}
\text{COO}^- & & \text{CO} & & \text{OC}\diagdown_{\!O} & & \text{COO}^- \\
| & & |\diagup^{\!O} & & | & & | \\
\text{HC—Br} & \longrightarrow & \text{H—C} & +\ \text{Br}^-; & \text{H—C} & +\ \text{H}_2\text{O} \longrightarrow & \text{HCOH} \\
| & & | & & | & & | \\
\text{HC—H} & & \text{H—C—H} & & \text{H—C—H} & & \text{HCH} \\
| & & | & & | & & | \\
\text{COO}^- & & \text{COO}^- & & \text{COO}^- & & \text{COO}^-
\end{array}
$$

In the case of formation of dibromosuccinic acid the reaction is not so easily followed. However, the existence of lactone in the product should be looked for.

The speed of rearrangement of the intermediate ion of the salt should be much less than that of the intermediate ion of the acid so that, other things being equal, there is a better chance for the union of the intermediate ion of the salt with chlorine ion, etc., *prior* to rearrangement, than in the case of the acid. The attractive force that brings about union of ions, Stage III, is always the same, since the static charges involved are the same. Hence, a light group such as hydroxyl should be brought to the heavy intermediate ion much more rapidly than the heavy bromine ion. Hence, *cis* addition should be favored the lighter the group to be added.
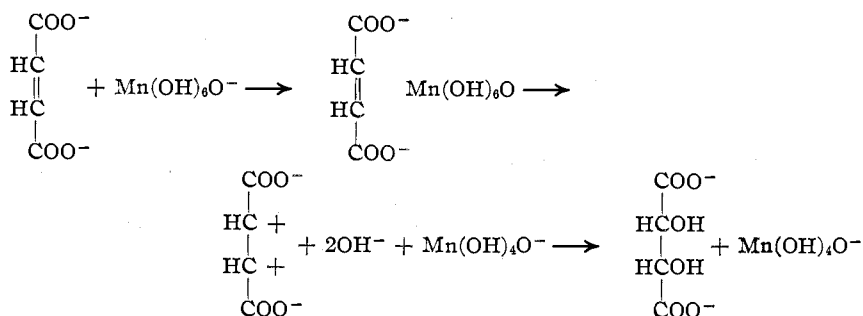
Since the rearrangement must involve work done either against or with the help of the influence of the adjacent groups, it is to be presumed that rearrangement which goes to form the more stable (*meso*) form of the isomers should be the swifter and the more difficultly controlled. This is the explanation offered by the theory for the fact that bromination of sodium maleate yields mainly *cis* addition product, but bromination of sodium fumarate yields mainly *trans* addition product.

The picture of the reaction of halogen and double bond as that of association of double bond and halogen, discharge of electrons, and union of unlike charged parts, therefore, accounts for the three fundamental observations given above in the summary of the experimental facts.

The Permanganate Reaction.—The theory accounts for the permanganate oxidation in the same terms as the halogenation. First, association occurs between permanganate ion or molecule with maleate or fumarate ion, then a discharge of electrons follows. Union of unlike charged ions then takes place, hydroxyl going at once to carbon and no intermediate

[13] Holmberg, *J. prakt. Chem.*, [2] 87, 456 (1913). Senter, *Ber.*, 45, 2378 (1912).

primary valence compound precedes the formation of tartaric acid. The stages of the reaction are shown below.[14] The heavy manganese ion would

$$
\begin{array}{c}
\text{COO}^- \\
| \\
\text{HC} \\
\| \quad + \text{Mn(OH)}_6\text{O}^- \longrightarrow \\
\text{HC} \\
| \\
\text{COO}^-
\end{array}
\qquad
\begin{array}{c}
\text{COO}^- \\
| \\
\text{HC} \\
\| \quad \text{Mn(OH)}_6\text{O} \longrightarrow \\
\text{HC} \\
| \\
\text{COO}^-
\end{array}
$$

$$
\begin{array}{c}
\text{COO}^- \\
| \\
\text{HC} + \\
| \quad + 2\text{OH}^- + \text{Mn(OH)}_4\text{O}^- \longrightarrow \\
\text{HC} + \\
| \\
\text{COO}^-
\end{array}
\qquad
\begin{array}{c}
\text{COO}^- \\
| \\
\text{HCOH} \\
| \quad + \text{Mn(OH)}_4\text{O}^- \\
\text{HCOH} \\
| \\
\text{COO}^-
\end{array}
$$

be beaten in the race to the positive carbon by the light hydroxyl ion. It should be noticed that the intermediate carbon ion is the same as in bromination.

**Oxidation of Fumaric and of Maleic Acids by Osmic Acid.**—In 1913, K. A. Hofmann[15] showed that a mixture of potassium chlorate and osmic acid oxidized sodium acid maleate or sodium acid fumarate in water solution to *meso* and racemic tartaric acids, respectively. Recently Milas and Terry[16] have perfected the control of this process so that 96% yields may be obtained. Whether the actual oxidizing agent is an intermediate compound of osmic acid and potassium chlorate, or simply osmic acid alone, which is reoxidized by potassium chlorate, is of no moment. The group added is the hydroxyl group so that *cis* addition should and does occur just as it does in the case of the permanganate reaction.

We may generalize that in all cases of oxidation of the double bond the mass of the molecule of the oxidizing agent is of no moment in determining whether or not a change of configuration will occur in addition. Only the weight of the group actually added to form the primary valence compound need be considered.

**Other Data on Halogenation of the Double Bond.**—A review of the literature of the other unsaturated carboxylic acids was undertaken for the purpose of securing other material for testing our theory. There was nothing to be found on the formation of dihalogen products in neutral

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[14] The formula of permanganate ion used requires explanation. As has been stated already, tartaric acid is the primary product of the reaction. According to our experience in the development of the theory, the hydroxyl must be present in the reaction association group. Hence, we have chosen to use the hydrated formula of permanganic acid. We have not hesitated to depict the association of two negative ions. Chemists are familiar with the formation of complex ions of the type of ferro- or ferricyanide. We do not wish to suggest any similarity in structure here, but merely to point out an example of the building up of a complex in which negative ions must have united.

[15] Hofmann, Ehrhardt and Schneider, *Ber.*, **46**, 1657 (1913).

[16] Unpublished results.

solution.   To be sure, we should not expect in the case of monocarboxylic
acids to achieve as good a control of the situation as with the dicarboxylic
acid.   A very fine review of the literature is given by Frankland.[17]   In
this he shows that, as a rule, halogen addition to the double bond is a *trans*
addition process.   The usual procedure is to halogenate in non-aqueous
solvents where, of course, this is to be expected.   However, the whole
situation is confused, for except in the case of fumaric and maleic acids,
the comparative structures of the isomers have not been established beyond
question.   Furthermore, it has been usual to report proportions of isomers
to each other and not the total yields of isomers.

**Validity of the Theory.**—Since in the above diverse and complicated
experimental conditions, the theory defines correctly the number of vari-
ables that control the experimental results, it has been presented.   It
cannot be said to have been proved to be true.   The idea of association
prior to change is, of course, a very old one.   The new idea is that re-
arrangement is brought about as the result of the influence of charges on ad-
jacent carbon atoms.   It is obvious that the mechanism described should
be operative in any change involving oxidation of an unsaturated group;
for example, bromination of conjugated bond compounds in general, etc.

**Walden Inversion.**—Other workers have anticipated that the phe-
nomena of bromination of fumaric and maleic acid have much in common
with the so-called Walden inversion.   This we believe to be the case.
By the Walden inversion is understood that curious series of reactions
by which an optically active substance undergoes substitution at the asym-
metric carbon atom to form either of two optically active products ac-
cording to the conditions of experiment.   Thus *l*-monochlorosuccinic
acid can be made to form either *d*- or *l*-malic acid on hydrolysis.   In nearly
all reports, one of the two processes is accompanied by the formation of
an unsaturated body.   Fumaric acid is found in the case of halogeno-
succinic acid.   Thus, in one of the two processes, the adjacent carbon
atom is active, and is probably the cause of the directed change.[18]

[17] Frankland, *J. Chem. Soc.*, **101**, 678 (1912).

[18] In the case of halogen succinic acid, it can be shown that an intermediate ion of the
structure indicated in Fig. 2 is probably formed.   The opposite charges appear in trans-
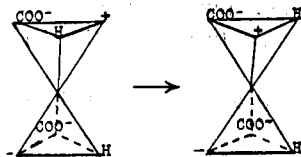


Fig. 2.

positions.   Rearrangement is possible only where movements of electrons are possible,
namely, on the alpha carbon.   Hence, a change of structure occurs before ions are picked
up to complete the compound.   If they fail to reach the intermediate ion in time, fu-

## Details of Experiments

We take pleasure in acknowledging that much of the fumaric and maleic acids used in this work was given us by the Barrett Company of New York, and that this courtesy was arranged for us by Messrs. Weiss and Downs, who were then with that company.

**Fumaric Acid.**—Fumaric acid was recrystallized from boiling water. Samples dried in a vacuum over sulfuric acid were found to melt at 285° in a sealed tube. The purity was also established by titration of a weighed sample.

**Maleic Acid.**—Maleic acid from the Barrett Company was purified by converting it into the anhydride as follows. The acid was mixed with 70% of its weight of phosphorus pentoxide in a distilling flask. The mixture was melted and then vacuum-distilled at 100–110°. The anhydride obtained was recrystallized from chloroform; final melting point, 53°; yield, 99%. Titrations of weighed quantities gave results as expected for the pure substance. We call attention to this method of preparation, since we have found it more efficient than any reported in the literature.

**Other Chemicals.**—Other chemicals used were the usual c.p. grades offered on the market.

**Hydrochloric Acid.**—Acid standards were made by the silver chloride precipitation method. By comparison, we found that we could use our own pure fumaric acid as standard acid. This confirms the report of Lange and Kline[19] on this acid as a standard acid. Since fumaric acid crystals are very light and have a tendency to "creep," they must be handled with special care.

We found it convenient to use, as weighing tubes, tiny U-tubes made of 6 mm. tubing and about 2 cm. in length. After a weighed sample had been taken in the usual way, the ends of the tube were sealed with drops of paraffin. In this manner a number of weighed samples could be made up at one time and stored ready for use. To standardize the base, the prepared tube was dropped into 50 cc. of hot water; the paraffin ends melted and the acid dissolved quickly. The base was then added as usual and the titration completed with phenolphthalein as indicator.

### Recovery and Identification of the Dibromosuccinic Acids.—After

a bromination was complete, the solution was acidified, and the halogen acids were extracted with ether. Weighed samples of the residue were titrated to determine the possible presence of unused fumaric or maleic acid. *iso*Dibromosuccinic acid is very much more soluble than the dibromo acid in water, and can be removed from the latter by washing with water. The water solution is then extracted with ether, the ether evaporated at ordinary temperature, and the residue treated with chloroform in which the dibromo acid or fumaric or maleic acid is little soluble. The residue from the chloroform solution has the decomposition point of pure *iso*dibromo acid.

### Recovery and Identification of the Dichlorosuccinic Acids.—These

maric acid results. The full argument is left to another paper. We are at present engaged in a review of the hydrolysis of phenylchloro-acetic acid which is alleged to undergo a Walden inversion. In the case of this acid, there could form no such intermediate ion, and it is probable that the optically active product reported in the literature is not mandelic acid. If it proves to be so, a new force is operative which is now unknown to us.

19 Lange and Kline, THIS JOURNAL, **44**, 2709 (1922).

acids were recovered from the reaction mixture in the same way as were the dibromo acids. The acids recovered from the sodium fumarate reaction melted at 168–173° with decomposition. This product was then crystallized from water, and the successive fractions were dried and their melting points observed. Although three fractions were taken, the decomposition points were the same for all. The same sort of experience was had with the acid from the chlorination of sodium maleate. In this case the melting point (with decomposition) was 214–218°. For comparison, a known mixture, 1.33 g. of each of the two isomers, was fractionally crystallized, and the melting points were taken of each fraction and of the dried residue. A second mixture of 4 g. of the *iso* and 1 g. of the dichloro acid was treated in the same way. Both experiments are reported herewith in tabular form.

| | Expt. I | | | Expt. II | |
| Fraction | Wt. G. | M. p. °C. | Fraction | Wt. G. | M. p. °C. |
| --- | --- | --- | --- | --- | --- |
| I | 0.6 | 218 | I | 0.4 | 212 |
| II | .75 | 210 | II | 2.0 | 168 |
| Residue | 1.0 | 168 | Residue | 2.1 | 173 |

It was clear, therefore, that had the products of the chlorination of the salts in question been mixtures of the isomers, fractional crystallization would have brought about a separation. Since the weighed samples of recrystallized acid titrated as would be expected if they were pure dichlorosuccinic acids, the proof was complete that the product of chlorination of sodium fumarate was *iso*dichlorosuccinic acid, and the product from the chlorination of sodium maleate was dichlorosuccinic acid. In each case, only negligible amounts of the other isomer could have been present and escaped detection.

**Identification of the Structure of the Isomeric Dihalogen Acids.—** The structure of the dibromo acids was finally established by McKenzie[20] and by Holmberg[21] separately. They were able to resolve the alkaloid salts of the *iso* acid into optically active components, but could not do so in the case of the dibromo. The *iso* is, therefore, the racemate and the dibromo the *meso* form. Similarly Holmberg[7] has resolved *iso*dichlorosuccinic acid into its components by the use of *d*,*α*-phenylamine. We are, therefore, certain that the dichloro acids have the structures of the corresponding dibromo acids.

## Summary

1. Soluble neutral salts of maleic acid, namely, the potassium, sodium, calcium, and strontium salts, treated in water solution with bromine in the presence of an excess of bromide ion, add bromine to form chiefly the *cis* addition product, namely, the salt of dibromosuccinic acid.

[20] McKenzie, *Proc. Chem. Soc.*, 27, 150 (1911); also *J. Chem. Soc.*, 101, 1197 (1912).
[21] Holmberg, *C. A.*, 6, 2072 (1912).

2.   When soluble neutral salts of fumaric acid are treated with bromine in the presence of an excess of bromide, mainly *trans* addition product forms; that is, the respective salts of dibromosuccinic acid.

3.   When soluble neutral salts of maleic acid are treated with chlorine in the presence of an excess of chloride ion, *cis* addition of chlorine occurs exclusively, and the result is that the salts of the dichlorosuccinic acid are formed.

4.   When soluble neutral salts of fumaric acid are treated with chlorine in the presence of sodium chloride, *cis* addition of chlorine takes place, and salts of sodium *iso*dichlorosuccinic acid are formed.

5.   A new method is reported for preparing maleic anhydride from maleic acid.

6.   The effect of the added bromide ion or chloride ion, summarized in Paragraphs 1 to 4, is to repress the formation of hypohalous acid so that halogen malic acids are not the product, as would otherwise be the case. This constitutes a new use of familiar reagents.   In the case of chlorination, the method reported is an important, new method of preparation, since heretofore the substances in question have been prepared with liquid chlorine—a very troublesome reagent.   The preparation of dibromosuccinic acid by the bromination of the neutral salt of maleic acid in the presence of an excess of bromide ion is mechanically simpler than the preparation of this acid by the bromination of fumaric acid in water or in acetic acid, the two methods heretofore used, and owing to the very great solubility in water of any residual maleic acid or of the *iso*-dibromosuccinic acid, made with the dibromo acid, the product is easily secured in pure form.

7.   A theory of the oxidation of the double bond is described which shows a possible source of the force which brings about a change of structure during addition.   It is indicated that a closely similar mechanism is probably responsible for the changes in configuration which occur in the Walden inversion.

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