800. *Mechanism of Elimination Reactions. Part XXI.** *Anomalous Elimination from αα′-Dichlorosuccinic Acid.*

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The kinetics and products of alkaline and acid aqueous monodehydrochlorination of *meso*- and racemic dichlorosuccinic acid are studied, and indications in the previous literature (which is corrected in some points) that the *meso*-acid breaks the stereokinetic rule of bimolecular *anti*-elimination are confirmed. An explanation is offered, which is based on non-synchronous timing in concerted *E*2 bond-changes, the impairment of simultaneity being in this case a relative advancement of deprotonation, due to the potential prototropy imported by the carboxyl groups.

The literature of olefin eliminations in simple systems contains a very few cases—only two unrevised ones, as far as we are aware—in which the main elimination product is the " theoretically incorrect " stereo- or position isomer. We look into these two qualitative anomalies in this and the following paper. We confirm both, and ascribe them, as we would ascribe several less striking, only quantitatively detectable deviations from expectation based on simple theory, to non-synchronous timing in concerted *E*2 bond-changes, as discussed, in the latter type of context, in Section 9 of Part XX.*

The qualitative anomaly of longest standing arises in connexion with the alkaline and acid aqueous monodehydrochlorination of *meso*- and racemic dichlorosuccinic acid. The literature of these reactions, which dates from 1892, contains a number of inconsistencies; but, through all, the report persists that both dichloro-acids in both sorts of conditions give wholly or largely chlorofumaric acid. It is reported also that the alkaline eliminations are second-order reactions. Bimolecular *anti*-elimination requires that the *meso*-dichloro-acid should give chloromaleic acid only, and that the racemic dichloro-acid should give chlorofumaric acid only.

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* Part XX, preceding paper.

As regards the reactions with aqueous hydroxide ion, Michael and Tissot[1] showed that the *meso*-dichloro-acid gave chlorofumaric acid, and Holmberg[2] showed that the racemic dichloro-acid gave the same product. Holmberg[3] found that both alkaline eliminations followed a second-order rate law, Rate $\propto$ $[OH^-][C_2H_2Cl_2(CO_2^-)_2]$, and that the reaction of the racemic acid went in his conditions about 9 times faster than did that of the *meso*-acid. Robinson and Lewis,[4] however, found no definite rate-law for the alkaline reaction of the racemic dichloro-acid, calculated second-order constants falling strongly with time. They suggested, but recorded no attempt to prove, that this acid becomes partly converted into the *meso*-acid during dehydrochlorination.

Concerning dehydrochlorination in aqueous acidic conditions, Michael and Tissot[1] showed that, when the *meso*-dichloro-acid was heated in water, a mixture of chloromaleic and chlorofumaric acid resulted, but that, when the racemic dichloro-acid was similarly treated, only chlorofumaric acid was produced. Holmberg[2] showed that these results remained unaltered when the reactions were conducted in the presence of added hydrochloric acid. Robinson and Lewis[4] reported, on the other hand, that acid dehydrochlorination of the *meso*-dichloro-acid gave chlorfumaric acid only. As to rate, Holmberg[3] found that acid dehydrochlorination of both dichloro-acids, both in the absence and in the presence of added hydrochloric acid, obeyed the first-order law, Rate $\propto$ $[C_2H_2Cl_2(CO_2H)_2]$, the reaction of the racemic dichloro-acid proceeding about 2·5 times faster than that of the *meso*-isomer. Robinson and Lewis,[4] however, found no definite rate-law for the acid dehydrochlorination of the racemic dichloro-acid, their calculated first-order constants falling with time.

Our revision completely confirms the earlier work, and traces all discrepancies to inaccuracies in Robinson and Lewis's. We assume that their supposed racemic dichloro-acid contained a large proportion of the *meso*-acid, and that they missed the more soluble isomer in the dehydrochlorination product whenever two isomers were formed.

We add some further particulars concerning the alkaline reactions. Both dichloro-isomers as sodium salts reacted with aqueous sodium hydroxide with good second-order rates, giving no indication of consecutive reactions. Comparison of the rate constants obtained in different runs disclosed a large positive salt-effect, controlled essentially by the ionic strength, as was confirmed by conducting runs not only with different initial concentrations of the reactants, but also with added sodium perchlorate or sodium chloride. The rate constants remain good, because the ionic strength does not change during a run. A large positive salt effect is expected for a reaction between ions of like charge. At 25°, the racemic dichloro-acid reacted 14 times faster than the *meso*-acid. The Arrhenius activation energy of the former reaction, 16·1 kcal./mole, was comparably lower than that of the latter, 17·4 kcal./mole, the difference accounting for a rate ratio of 9.

In these reactions, Holmberg, and also Johansson, found[3] rates which were 2—3 times greater when the alkali was barium hydroxide than when it was sodium or potassium hydroxide. We confirmed the difference. We explain it by assuming that the dichlorosuccinate ions and the barium ions partly associate, as multivalent ions are known to do in water, and that the cationic field in the ion-pairs locally breaks down the electrostatic opposition to encounters between the dichlorosuccinate and hydroxide ions.

We confirm that the second-order reactions of both *meso*- and racemic dichlorosuccinate ion with hydroxide ion give one and the same monodehydrochlorination product, the chlorofumarate ion. We isolated chlorofumaric acid in pure form and in high yield. We confirmed that chloromaleic acid is stable under the conditions of production of the chlorofumaric acid, and, if formed at all, would survive and be detected.

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[1] Michael and Tissot, *J. prakt. Chem.*, 1892, **46**, 392; 1895, **52**, 333; cf. van der Riet, *Annalen*, 1894, **280**, 228.

[2] Holmberg, *Arkiv Kemi, Min., Geol.*, 1920, **8**, no. 2.

[3] Holmberg, *J. prakt. Chem.*, 1911, **84**, 149; *Z. phys. Chem.*, 1912. **79**, 147; cf. Johansson, *ibid.*, p. 625.

[4] Robinson and Lewis, *J.*, 1933, 1260.

The more difficult of these results to understand is that the *meso*-dichloro-acid gives only chlorofumaric acid. Skell and Hauser's test for a prior-deprotonation mechanism was therefore applied in this case, by conducting the reaction in deuterio-water, and looking for deuterium in starting material recovered after partial conversion. The uptake of deuterium was only about 0·5% of that possible. Cristol and Fix [5] obtained a deuterium uptake of the same order of magnitude in a similar experiment on the alkaline dehydrochlorination of β-benzene hexachloride, and regarded it as supporting the prior-deprotonation mechanism, *E*1c*B*. We do not think that our observed uptake of deuterium is sufficient to support any conclusion about the mechanism of the main reaction.

We next fill in some details concerning the acid dehydrochlorinations. Both the dichloro-acids in water alone underwent dehydrochlorination with good first-order rates. Addition of sodium perchlorate disclosed a small negative salt-effect. Additions of perchloric acid in small concentrations reduced reaction rate rather more than the equivalents of sodium perchlorate would have done; but at higher concentrations of perchloric acid, such as N, further perchloric acid and sodium perchlorate reduced the rate slightly and similarly. We think it possible that the dichloro-acids react with water in the absence of an added strong acid both in their undissociated forms and as their monoanions, and that the first effect of an added strong acid is to suppress the monoanions, leaving in isolation, above a certain acidity, only the reactions of the molecular acids. Because these have small negative salt effects, and no large positive ones, we assume that they are bimolecular reactions, *E*2 essentially, with water as the basic reagent, rather than unimolecular eliminations, *E*1. In N-aqueous perchloric acid at 80°, the racemic dichloro-acid underwent dehydrochlorination 2·7 times faster than the *meso*-acid. The Arrhenius activation energy of the former reaction, 22·1 kcal./mole, was comparably lower than that of the latter, 22·5 kcal./mole, the difference accounting for a rate-ratio of 1·8.

The reaction of *meso*-dichlorosuccinic acid, both in water alone, and in water containing N-perchloric acid, gave mixtures of chloromaleic and chlorofurmaric acid, which, separated from non-isomers in good yield, were analysed by a kinetic method. Such a mixture, produced in the less acidic conditions, contained 61% of chloromaleic and 39% of chlorofumaric acid. Another mixture, formed in the more strongly acid conditions, contained 53% of chloromaleic acid and 47% of chlorofumaric acid. The reaction of racemic dichlorosuccinic acid, both with water alone, and with water containing N-perchloric acid, gave only chlorofumaric acid, which was isolated in a pure form and in high yield. It was shown that chloromaleic acid was stable under the various conditions of production of chlorofumaric acid and of the mixed isomers, *i.e.*, that the unsaturated acids obtained are original dehydrochlorination products.

To interpret these relations, we shall assume that all the eliminations considered are *E*2 in mechanism, whether the substrate is a dichlorosuccinate ion or the corresponding acid molecule, and whether the involved base is a hydroxide ion or a water molecule. We shall also assume that the substrates are stable only in staggered conformations, and, among these, most stable in those having *anti*-carboxyl groups.

The reactions of the racemic dichloro-ion and molecule appear straightforward. Of the three conformations, (I)—(III), the *anti*-carboxyl one (III) is not only the most stable, but also the only one with an *anti*-HCl atom-pair, as needed for ready *E*2 elimination. The result of this elimination must be to give chlorofumaric acid, which in fact is the only isomer formed, either in alkaline or acid conditions.

The possibilities before the *meso*-dichloro-ion and -molecule are less obvious. Of the three conformations (IV—VI), only (VI) is stable, but it has not the *anti*-HCl arrangement needed to facilitate *E*2 elimination. The usual result of such a situation would be that elimination would occur more slowly through some unstable conformation; but in this case, the prototropy, imported into the molecular system by its carboxyl groups, may

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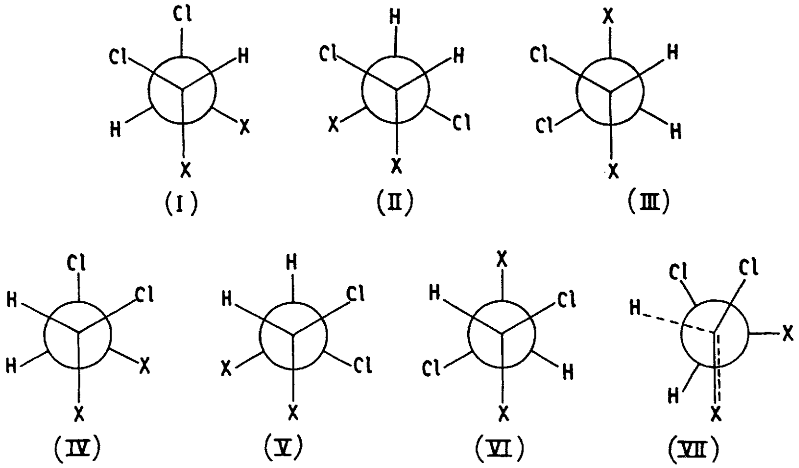
[5] Cristol and Fix, *J. Amer. Chem. Soc.*, 1953, **75**, 2647.

provide an easier alternative. The effect of the potential prototropy would be, not necessarily to break up the concerted character of the *E*2 bond-changes, but certainly to impair their near-simultaneity, (*a*) by facilitating and advancing deprotonation, and (*b*) by providing a special reservoir for the electrons thus liberated. This will have stereochemical consequences. For, as the proton is loosened, most of the charge it leaves on carbon will be transferred to oxygen; and that transfer will be instantaneous on the time-scale of nuclear movements. Thus it transpires that enolic $C{=}C$ electrons rather than original CH electrons, have to assist the departure of the halide ion, and must be *anti*-related to the separating halogen in order to fulfil this function. Accordingly, the transition state will become modified towards the *E*1*cB*-like form (VII), in which a partly enolised carboxyl group is approximately *anti*-related to a chlorine atom. The formula suggests the production of comparable amounts of chloromaleic and chlorofumaric acid, as, indeed, is observed in acid dehydrochlorinations of the *meso*-dichloro-acid. It is then easy to understand how, in the corresponding alkaline dehydrochlorination, in which the groups X in (VII) are no longer the neutral groups, $C(OH)_2$ and CO_2H, but are the charged groups, CO_2^{2-} and CO_2^-, inter-ionic repulsion will conformationally twist the transition state in the sense favouring a more exclusive production of chlorofumaric acid, which, in fact, is the only observed product of the alkaline dehydrochlorination.

FIG. 1. *Conformations of dichlorosuccinic acids and anions.*



Racemic, I—III; most stable, III; transition state for elimination, like III.
Meso-, IV—VI; most stable VI; transition state for elimination, more like VII than VI.
$-X$ means $-CO_2H$ or $-CO_2^-$; $=X$ means $=C(OH)_2$ or $=CO_2^{2-}$.

EXPERIMENTAL

Materials.—*meso*-Dichlorosuccinic acid was prepared by Terry and Eichelberger's method [6] of adding chlorine to sodium maleate in a neutral aqueous solution saturated with sodium chloride. We agree with Kuhn and Wagner-Jauregg [7] that it is difficult similarly to prepare racemic dichlorosuccinic acid from sodium fumarate, because this reaction leads to both dichloro-acids, besides chloromalic acid, and the required racemic acid is intermediate in solubility between the other two acids. We therefore made it by Michael and Tissot's method [1] of leading chlorine into a solution of maleic anhydride in carbon tetrachloride in sunlight, and hydrolysing the resulting dichlorosuccinic anhydride. The *meso*-acid had m. p. 216—218° (decomp.) (Found: C, 25·8; H, 2·2; Cl, 37·9%; equiv., 93·5. Calc. for $C_4H_4Cl_2O_4$: C, 25·7;

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[6] Terry and Eichelberger, *J. Amer. Chem. Soc.*, 1925, **47**, 1067.
[7] Kuhn and Wagner-Jauregg, *Ber.*, 1928, **61**, 518.

H, 2·1; Cl, 37·9%; equiv., 93·5). The racemic anhydride had m. p. 94—95°, and the acid, m. p. 173—175° (decomp.) (Found: C, 25·8; H, 2·2; Cl, 37·8%; equiv., 93·5). Chlorofumaric acid, prepared by a method due to Perkin,[8] had m. p. 193°. Chloromaleic acid, obtained from the commercial anhydride, had m. p. 108—109°.

Kinetics.—Samples were withdrawn by pipette from the reaction solutions, the first sample, taken after the initial thermal disturbance was over, marking the time-zero, and were quenched by strong cooling. In alkaline runs, samples were titrated either for residual alkali, or by Volhard's method for liberated chloride ion, the two procedures giving the same results. Infinite-time readings were not taken, because the slow second step of dehydrochlorination was fast enough to spoil such measurements. Second-order rate-measurements were calculated from the usual formula, and corrected for thermal expansion of the solvent where necessary. Acid runs were followed by titrating the liberated chloride ion potentiometrically. First-order rate constants were calculated from the usual formula.

These kinetic laws held so exactly throughout this investigation, that we illustrate our runs minimally in Table 1 by an alkaline and an acid run with each dichloro-acid. In this and later

TABLE 1. *Alkaline and acid aqueous monodehydrochlorinations of* meso- *and racemic dichlorosuccinic acids: four illustrative runs.*

Run 15 : *Reaction of the* meso-*acid with sodium hydroxide in water at* 25·0°. (Initially, $[C_2H_2Cl_2(CO_2^-)_2]$ = $[OH^-]$ = 0·1020M. Samples of 10 ml. titrated with 0·0510N-HCl.)

t (hr.)	0·0	0·5	1·0	2·0	3·0	4·0	6·0	8·0	21·0
Titre (ml.)	20·08	18·35	16·90	14·65	12·78	11·46	9·49	8·02	3·98
10^5k_2	—	51·1	51·1	50·4	51·4	51·2	50·6	51·1	51·9
								Mean:	51·1

Run 88: *Reaction of the racemic acid with sodium hydroxide in water at* 25·0°. (Initially, $[C_2H_2Cl_2(CO_2^-)_2]$ = $[OH^-]$ = 0·0500M. Samples of 10 ml. titrated with 0·02034N-HCl.)

t (min.)	0	10	20	30	40	60	90	120	150
Titre (ml.)	22·07	19·40	17·31	15·65	14·21	12·09	9·85	8·43	7·20
10^5k_2	—	512	510	509	514	511	511	500	512
								Mean:	511

Run 125: *Reaction of the* meso-*acid with water containing* 0·974N-*perchloric acid at* 80·0°. (Initially, $[C_2H_2Cl_2(CO_2H)_2]$ = 0·0290M at 20°. Samples of 5·582 ml. at 20° titrated with 0·009979N-$AgNO_3$.)

t (hr.)	0	1	2	3	4	5	6	7	8
Titre (ml.)	0·35	1·47	2·53	3·52	4·41	5·26	6·05	6·78	7·46
10^5k_1	—	1·96	1·98	1·98	1·97	1·97	1·97	1·97	1·97
								Mean:	1·97

Run 129: *Reaction of the racemic acid with water containing* 0·974N-*perchloric acid at* 80·0°. (Initially, $[C_2H_2Cl_2(CO_2H)_2]$ = 0·0290M at 20°. Samples of 5·582 ml. at 20° titrated with 0·009979N-$AgNO_3$.)

t (hr.)	0·00	0·25	0·50	0·75	1·00	1·25	1·50	1·75	2·00
Titre (ml.)	0·78	1·54	2·24	2·89	3·53	4·15	4·74	5·29	5·81
10^5k_1	—	5·39	5·31	5·23	5·25	5·26	5·28	5·28	5·25
								Mean:	5·28

Tables, k_2 is always in $sec.^{-1}$ $mole^{-1}$ l., and k_1 in $sec.^{-1}$. Tables 2—5 assemble the second- and first-order rate constants for the alkaline and acid runs of the *meso*- and racemic dichloro-acid.

Products.—The principal findings have been summarised and it remains only to illustrate methods.

As to the alkaline reactions, aqueous solutions of either dichloro-acid, along with a sufficient excess of sodium hydroxide to produce a solution 0·1M in both the dichlorosuccinate ion and hydroxide ion, were kept at 25° for ten " half-lives," acidified, and extracted with ether;

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[8] Perkin, *J.*, 1888, **53**, 695.

TABLE 2. *Second-order rate constants of reaction of the* meso-*acid with alkali hydroxide in water.*

Temp.	$[C_2H_2Cl_2(CO_2^-)_2]$	[NaOH]	$[NaClO_4]$	μ	10^5k_2 by OH^-	10^5k_2 by Cl^-
25·00°	0·102	0·102	—	0·408	51·1	50·0
,,	0·102	0·195	—	0·498	57·2	58·1
,,	0·102	0·296	—	0·602	65·8	67·2
,,	0·102	0·490	—	0·796	79·2	—
,,	0·077	0·190	—	0·421	51·4	—
,,	0·125	0·194	—	0·569	58·9	—
,,	0·172	0·197	—	0·713	73·7	—
,,	0·101	0·195	0·089	0·587	63·0	64·7
,,	0·101	0·195	0·089 *	0·587	63·6	63·8
,,	0·101	0·195	0·160	0·664	69·2	—
,,	0·101	0·195	0·302	0·800	81·1	—
,,	0·101	0·195	0·502	1·000	99·0	—
20·00	0·102	0·102	—	0·408	31·9	—
35·00	0·102	0·102	—	0·408	128	—
44·65	0·102	0·102	—	0·408	322	—
25·00	0·0788	[KOH] 0·0788	—	0·315	51·7	51·1
25·00	0·0271	$[Ba(OH)_2]$ 0·0135	—	0·149	189	185

* NaCl, not $NaClO_4$.

TABLE 3. *Second-order rate constants of reaction of the racemic acid with alkali hydroxide in water.*

Temp.	$[C_2H_2Cl_2(CO_2^-)_2]$	[NaOH]	$[NaClO_4]$	μ	10^5k_2 by OH^-	10^5k_2 by Cl^-
25·00°	0·050	0·050	—	0·200	511	511
,,	0·050	0·100	—	0·250	575	578
,,	0·050	0·150	—	0·300	620	610
,,	0·075	0·100	—	0·325	642	—
,,	0·100	0·100	—	0·400	736	—
,,	0·050	0·050	0·030	0·230	567	—
,,	0·050	0·050	0·080	0·280	622	—
,,	0·050	0·050	0·130	0·330	672	—
,,	0·050	0·050	0·180	0·380	742	—
19·95	0·050	0·050	—	0·200	328	—
30·00	0·050	0·050	—	0·200	830	—
34·71	0·050	0·050	—	0·200	1252	—
25·00	0·0303	$[Ba(OH)_2]$ 0·0151	—	0·167	1660	—

TABLE 4. *First-order rate constants of reaction of the* meso-*acid with water in acid solution.*

Temp.	$[C_2H_2Cl_2(CO_2^-)_2]$	$[HClO_4]$	$[NaClO_4]$	μ	10^5k_1 (by Cl^-)
80·00°	0·020	—	—	—	2·49
,,	0·030	—	—	—	2·55
,,	0·040	—	—	—	2·59
,,	0·060	—	—	—	2·65
,,	0·030	—	1·00	1·00	2·24
,,	0·030	0·100	—	—	2·45
,,	0·030	0·200	—	—	2·38
,,	0·029	0·974	—	0·97	1·97
,,	0·030	2·00	—	2·00	1·54
,,	0·030	3·00	—	3·00	1·225
,,	0·030	4·00	—	4·00	1·011
,,	0·030	1·00	1·00	2·00	1·460
,,	0·030	2·00	1·00	3·00	1·167
,,	0·030	3·00	1·00	4·00	0·915
65·42	0·029	—	—	—	0·552
,,	0·029	0·974	—	0·97	0·491
72·67	0·029	—	—	—	1·213
,,	0·029	0·974	—	0·97	1·000
87·44	0·029	—	—	—	5·19
,,	0·029	0·974	—	0·97	3·75

95—99% yields were obtained of material, m. p. 190° or just above, and similar mixed m. p.s with authentic chlorofumaric acid, m. p. 193° (Found: C, 31·9, 32·0; H, 2·1, 2·2; Cl, 23·5, 23·2. Calc. for $C_4H_3ClO_4$: C, 31·9; H, 2·0; Cl, 23·6%).

The stability of chloromaleic acid in these conditions was directly checked, though the point is indirectly covered by Cristol and Begoon's demonstration [9] that this acid is more stable to alkali than is chlorofumaric acid which we isolated. Robinson and Lewis's suggestion [4] that the racemic dichloro-acid is isomerised to the *meso*-dichloro-acid in the course of alkaline dehydrogenation was proved incorrect by isolating the product of a partial conversion of the racemic dichloro-acid, and showing, by a leaching-out method, elaborated with artificial mixtures of the two dichloro-acids and chlorofumaric acid, that the partly converted material contained no detectable amount of *meso*-acid.

Unconverted *meso*-acid was also recovered by leaching-out more soluble acids from the product of a partial alkaline dehydrochlorination of the *meso*-dichloro-acid in deuterio-water. It was assumed that the separation process would have isotopically normalised carboxyl-hydrogen. The sample, after ordinary analysis, was burnt, and the water was collected. This was reduced with zinc dust, and the hydrogen was analysed for deuterium content in the mass-spectrometer, with the result already noted.

TABLE 5. *First-order rate constants of reactions of the racemic acid with water in acid solution.*

Temp.	$[C_2H_2Cl_2(CO_2H)_2]$	$[HClO_4]$	$[NaClO_4]$	μ	10^5k_1 (by Cl^-)
80·00°	0·020	—	—	—	9·14
,,	0·030	—	—	—	9·08
,,	0·040	—	—	—	9·00
,,	0·060	—	—	—	9·00
,,	0·030	—	1·00	1·00	8·30
,,	0·030	0·100	—	—	7·70
,,	0·030	0·200	—	—	7·17
,,	0·029	0·974	—	0·97	5·28
,,	0·030	2·00	—	2·00	3·58
,,	0·030	3·00	—	3·00	2·54
,,	0·030	4·00	—	4·00	1·88
,,	0·030	1·00	1·00	2·00	3·52
,,	0·030	2·00	1·00	3·00	2·46
,,	0·030	3·00	1·00	4·00	1·76
65·42	0·029	—	—	—	1·91
,,	0·029	0·97	—	0·97	1·35
72·67	0·029	—	—	—	4·34
,,	0·029	0·97	—	0·97	2·70
87·44	0·029	—	—	—	19·8
,,	0·029	0·97	—	0·97	9·70

Acid dehydrochlorinations were run for the ten " half-lives " in water at 80° with both *meso*- and racemic dichlorosuccinic acid, and in both cases in the absence of strong acids, as well as in the presence of N-perchloric acid. From the product recovered after conversion of the racemic dichloro-acid in the absence of strong acids, an 80% yield of pure chlorofumaric acid was isolated, and identified, as in the alkaline dehydrochlorinations already described. The unseparated part of the product of this run was shown by catalytic hydrogenation to contain chloromalic acid equivalent to a 13% yield on the overall reaction. The figure is derived from the amount of hydrogen absorbed, on the basis that chlorofumaric acid takes up four atoms of hydrogen and chloromalic acid only two under the conditions used. Tartaric acid could not be detected. From the product of dehydrochlorination of the racemic dichloro-acid in the presence of N-perchloric acid, a 90% yield of pure chlorofumaric acid was isolated and identified, as before.

The products of the acid conversions of *meso*-chlorosuccinic acid, in either set of conditions, were obviously mixtures. From such a conversion in the absence of an added strong acid, an 87% yield was obtained of a binary isomer mixture, *i.e.*, a partly purified mixture, shown by its acid equivalent, its uptake of just four hydrogen atoms on catalytic hydrogenation, and its mixed-melting behaviour, to contain only chlorofumaric and chloromaleic acid. A further 9% of the dehydrochlorination product was recovered as a mixture of acids, which was shown by

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[9] Cristol and Begoon, *J. Amer. Chem. Soc.*, 1952, **74**, 5025.

hydrogenation to comprise a further 4% yield of elimination products (presumably chlorofumaric and chloromaleic acid), and a 5% yield of substitution products (probably mainly chloromalic acid), these figures being calculated on the basis that chlorofumaric and chloromaleic acid each take up four atoms of hydrogen and chloromalic acid two atoms, with no allowance for tartaric acid, which would take up none, because that acid could not be detected through its ferric salt. The 87%-sample of mixed isomers was analysed by a kinetic method, based on the fact [9] that chlorofumaric acid undergoes further dehydrochlorination in excess of alkali about 20 times faster than does chloromaleic acid. These analytical dehydrochlorinations were run in water at 25°, with the two pure acids and the analytical sample in parallel, using a ten-fold excess of 0·4N-sodium hydroxide, and following chloride liberation by potentiometric titration. The sample was thus shown to contain 39% of chlorofumaric acid and 61% of chloromaleic acid.

A similar examination was made of the product of conversion of *meso*-dichlorosuccinic acid in the presence of N-perchloric acid. The yield of the binary isomer mixture, as prepared for analysis, was in this case 85%. It was shown to contain 47% of chlorofumaric acid and 53% of chloromaleic acid.

The stability of chloromaleic acid in the conditions of the acid dehydrochlorinations, both in the absence and in the presence of perchloric acid, was checked by putting chloromaleic acid through those two procedures, after which it was recovered unchanged, practically quantitatively.

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