#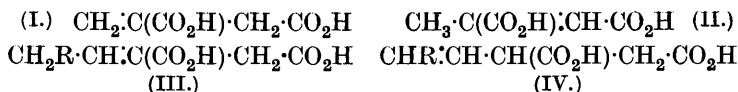 XCIX.—Investigations of the Olefinic Acids. Part IV. The Two Types of Tautomerism of Itaconic Acids and the Connexion between Configurational and Tautomeric Changes in Alkali.

By REGINALD PATRICK LINSTEAD and JASON THOMAS WILLIAM MANN.

IN extending the quantitative study of isomeric changes in unsaturated acids to the dibasic acid series we first selected the $\alpha\beta$-dicarboxypropenes (Type I)—the itaconic acids—for two reasons. First, of the other classes of simple dibasic acids, the $\alpha\alpha$ type—the unsaturated malonic acids—are comparatively unstable, and the glutaconic acids ($\alpha\gamma$ type) present a problem of greater complexity which is now receiving separate study in these laboratories. Secondly, in the itaconic series the $\alpha\beta$-unsaturated forms (Type II) and a few of the itaconic acids themselves exist in well-defined geometrical modifications about the double bond, thus making investigation possible on the connexion between the three-carbon changes and the geometrical inversion.

The possibilities of tautomeric change in the itaconic acids do not end with interconversions of the type I $\rightleftharpoons$ II, for it has been shown by Fittig and his co-workers that γ-alkyl itaconic acids (III) can be converted reversibly by boiling alkali into the corresponding aticonic acids (IV).

(I.) $CH_2\!:\!C(CO_2H)\cdot CH_2\cdot CO_2H$ $\quad$ $CH_3\cdot C(CO_2H)\!:\!CH\cdot CO_2H$ (II.)

$CH_2R\cdot CH\!:\!C(CO_2H)\cdot CH_2\cdot CO_2H$ $\quad$ $CHR\!:\!CH\cdot CH(CO_2H)\cdot CH_2\cdot CO_2H$

$\quad\quad\quad$ (III.) $\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad$ (IV.)

The present work describes quantitative investigations of both types of tautomerism and also of the configurational change and by correlating the results with those of previous workers we have been enabled to advance generalisations as to the factors governing these changes.

Type I.—The system itaconic acid (I)–citraconic acid (II, *cis*)–mesaconic acid (II, *trans*-) was selected owing to the availability of the materials. Previous work on the interconversion of these acids in alkali is to some extent contradictory. Delisle (*Annalen*, 1892, **269**, 74) examined the action of alkali under various conditions of temperature and concentration on the two forms of the $\alpha\beta$-acid. His results indicate the existence of an equilibrium between the three acids, the system then containing 57% of mesaconic, 17% of itaconic, and 26% of citraconic acid (by difference). The only other determinations are a few by Fittig and Lang-

worthy (*Annalen*, 1899, **304**, 145) which may be summarised by the statement that all three acids on treatment with boiling alkali yielded a mixture containing some 7 parts of mesaconic acid to 2 of itaconic. No citraconic acid was formed from its isomerides, although even after 24 hours' equilibration some of this acid could be recovered unchanged.

The discrepancy between these results is to be attributed mainly to analytical errors. Delisle gives no figures for the citraconic acid content of his equilibrated samples and the loss involved in his experiments is therefore unknown. His method for the elimination of citraconic acid must have led to loss of the other components, and the melting point of the material returned as itaconic acid indicates the presence in it of mesaconic acid. The analytical methods of Fittig and Langworthy appear to have been more accurate, although their loss averages 12%. The facts that Delisle definitely isolated citraconic acid by equilibration of mesaconic acid and Fichter (footnote to Fittig's paper, *loc. cit.*) also isolated it from itaconic acid, taken together with the results described below, make it very probable that the bulk of the loss in Fittig's experiments represents citraconic acid.

In the present work all three isomerides were equilibrated under conditions similar to those standardised for monobasic olefinic acids (Linstead, J., 1927, 2579). Methods were developed for the extraction and isolation of the equilibrated material, the accuracy of which was established by control experiments. The loss in the reaction and extraction averaged 3%, and that during separation about 5%. This gain in accuracy involved the use of an extremely tedious series of operations, each complete estimation requiring about a fortnight's work.

The analytical procedure is described in the experimental section. Comment is only necessary on the use of steam distillation for the separation of the citraconic acid, since the published evidence as to the volatilities of the three acids in steam is contradictory. Franz (*Monatsh.*, 1894, **15**, 209) reports that citraconic acid is largely but not completely volatile in steam, whereas both mesaconic and itaconic acid are slightly volatile. Fittig (*loc. cit.*), however, states that citraconic acid can be separated completely from mixtures of the three acids by steam distillation without the removal of any of the isomerides. Preliminary experiments confirmed Fittig's results, but it was found that the volatility in steam of citraconic acid (or, rather, its anhydride) falls with its concentration in the solution under distillation to such an extent that large amounts of water are necessary for complete separation (*e.g.*, 6 litres for 5 g.). Under these conditions itaconic acid is

non-volatile and mesaconic acid very slightly volatile in steam. A feature of interest is that when pure citraconic acid or mixtures containing it are so distilled, extraction of the distillate yields the acid always contaminated by traces of an oily impurity, possibly methacrylic acid.

The results of the equilibrations, expressed in round figures as percentage compositions, are in Table I, and the full data on p. 736.

TABLE I.

Equilibration of Citraconic, Mesaconic, and Itaconic Acids.

% Composition of Product.

Expt. No.	Acid used.	Time of treatment (mins.).	Volatile in steam. (Citraconic acid).	Non-volatile in steam.		% Loss.
				Mesaconic acid.	Itaconic acid.	
1	Citraconic	5	78	5	11	6
2	,,	7	72	10	13	5
3	,,	14	57	19	16	8
4	,,	30	45	37	18	0
5	,,	65	21	58	15	6
6	,,	120	14	65	16	5
7	,,	360	11	69	16	4
8	,,	1440	11	70	14	5
9	Mesaconic	7	2	87	8	3
10	,,	40	10	74	13	3
11	,,	120	12	68	14	6
12	Itaconic	7	11	35	47	7
13	,,	20	13	64	18	5
14	,,	31	17	66	15	2
15*	Citraconic	540	43	35	16	6

* This experiment was carried out at 75°.

These results show with certainty that a true equilibrium is reached from all three acids. Contrary to Fittig's statement, the equilibrium mixture contains citraconic acid and its true composition is considered to be : citraconic acid, 15%; mesaconic acid, 69%; itaconic acid, 16%. The proportion of citraconic acid has here been raised slightly from that actually found, as experiments on the pure acids indicate that the analytical loss occurs mainly at the expense of this component. The equilibrium value of 84% $\alpha\beta \rightleftharpoons 16\%$ $\beta\gamma$ is attained very rapidly, the system, regarded as a simple three-carbon system, being the fastest yet measured among unsaturated acids. The mobility is not a true one, as the $\alpha\beta$–$\beta\gamma$ change is not simple, but its order is indicated by the approximate figures from the $\beta\gamma$-side : time of half-change, 6 minutes; mobility, 69. The change from mesaconic acid is approximately equal in speed, that from citraconic acid considerably faster (mobility, ca. 140).

The internal configurational equilibrium of the $\alpha\beta$-acid is reached

more slowly at a value of 18% *cis*- acid $\rightleftharpoons$ 82% *trans*-. Itaconic acid gives this value much more rapidly than does either form of the αβ-acid. The mechanism of the stereochemical change of the αβ-acid may be discussed now in order to simplify the subsequent review of the purely tautomeric side. The figures show clearly that both forms of the αβ-acid are capable of direct conversion into the βγ-acid, and it only remains to decide whether the configurational change takes place entirely through the intervention of this form or whether " triangular " equilibration can take place :

$$\beta\gamma$$
$$\diagup \qquad \diagdown$$
$$cis\text{-}\alpha\beta \rightleftharpoons trans\text{-}\alpha\beta.$$
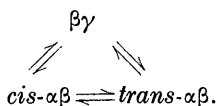
Although the possibility of the operation of the second process cannot be entirely excluded, the available evidence strongly supports the view that under the experimental conditions *configurational change in the αβ-acid proceeds entirely through the intermediate formation and decomposition of the βγ-isomeride ;* a study of changes in related compounds gives no indication that direct geometrical inversion occurs in alkali when the tautomeric mechanism is available. Further, when no tautomerism is possible, the velocity of the stereochemical change is greatly reduced. With " direct " inversions must be included such possible modes of change as that involving reversible addition of catalysts.

The internal evidence in support of these contentions is : (*a*) configurational equilibrium is reached more rapidly from the βγ- than from either form of the αβ-acid. (*b*) The initial formation of citraconic acid from mesaconic acid is slow and that of mesaconic acid from citraconic acid is both slow and irregular, as much being produced between 5 and 7 minutes as in the first 5 minutes. As soon as the concentration of the itaconic acid formed from the citraconic acid reaches the equilibrium value, however, the formation of mesaconic acid proceeds regularly with respect to time. (*c*) There is an indication of a " peak " in the production of itaconic acid from citraconic acid, and it may be inferred that, but for the intervention of the " drain " to mesaconic acid, the real value for the equilibrium *cis*-αβ $\rightleftharpoons$ βγ-acid would be further on the βγ-side than that found for the complete system. Additional support for this view comes from Delisle's observation (*loc. cit.*) that aqueous sodium citraconate, heated for 6 hours at 170°, gave an 8% conversion into the itaconic salt without perceptible formation of mesaconate.

No collateral evidence is available from the chemistry of monobasic unsaturated acids, although several of these are now under

investigation from this point of view, but among dibasic acids a suggestive comparison may be drawn between the geometrical inversion of citraconic acid in alkali and that of its higher and lower homologues. Fittig and Kettner (*Annalen*, 1898, **304**, 156) showed that the three-carbon equilibrium
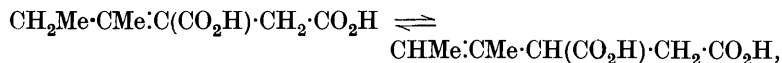
$$CH_2:C(CO_2H)\cdot CHMe\cdot CO_2H \rightleftharpoons CH_3\cdot C(CO_2H):CMe\cdot CO_2H$$
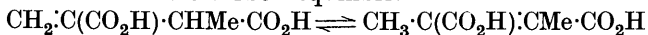
is rapidly reached from the *cis*-αβ-acid (or, actually, its anhydride) under conditions when as little as 2% of the fumaroid form is produced and, further, that a "peak" amount of βγ-acid can thus be obtained. The configurational change is here considerably slower than for citraconic acid, but 34% of the *trans*-αβ-acid is formed from the *cis*-anhydride by 10 hours' boiling with 30% alkali solution. With maleic acid itself, however, the change is not only slow but difficult to observe. For instance, Loydl (*Annalen*, 1878, **192**, 80) and van 't Hoff (*Ber.*, 1885, **18**, 2713) obtained the hydroxy-acid, *dl*-malic, from fumaric and maleic acids respectively without observing any geometrical inversion, although Skraup (*Monatsh.*, 1891, **12**, 115) states that maleic acid gives rise to the formation of "a not insignificant" amount of fumaric acid under Loydl's conditions. Delisle (*Annalen*, 1892, **269**, 76) showed that, although no fumaric acid was formed by the action of alkali on maleic acid at 100°, a slow change of this type occurred at 106° leading to the production, in 12 hours with 30% alkali solution, of $3\frac{1}{2}\%$ of the *trans*-acid. He further showed that under the same conditions malic acid itself decomposed at about the same rate into fumaric acid.

There is, therefore, clear indication that, when the tautomeric mechanism is not available, the comparatively slow and inefficient process of reversible addition of water has to be utilised to effect the stereochemical change. It is well known that changes of *cis*- to *trans*-acids, proceeding through some form of additive mechanism, are usually irreversible, and it may well be a criterion of changes involving a tautomeric mechanism that they enable the *trans*- ⟶ *cis*-change to proceed. The comparative ease of stereochemical change in mobile tautomeric systems should account for the difficulty of isolation of many of the unstable forms of the glutaconic acids (compare Packer and Thorpe, J., 1926, 1199) and in this connexion it is of interest that the allied phenomenon of optical inversion in the glutaconic series is attributed to tautomeric change by McCombs, Packer, and Thorpe (this vol., p. 547), who correlate the rapid racemisation of *l*-αγ-dimethylglutaconic acid with the high tautomeric mobility of the system.

Type II.—Whereas the principal features of the tautomerism of itaconic acids without a γ-substituent can be summarised as

high mobility and occurrence of stereoisomeric changes, those of γ-alkyl itaconic acids are exactly the reverse : the change is extremely slow and stereoisomerides are not encountered. The system of this type studied was that of the γ-methyl-γ-ethyl-itaconic and -aticonic acids (V and VI),

$$CH_2Me \cdot CMe \vdots C(CO_2H) \cdot CH_2 \cdot CO_2H \; \rightleftharpoons$$
$$CHMe \vdots CMe \cdot CH(CO_2H) \cdot CH_2 \cdot CO_2H,$$

which were selected in the hope that the aticonic acid might prove more stable to boiling alkali solution than the acids of its type examined by Fittig. This hope was realised, and the acid (VI) is, in fact, the first acid of its class found to be more stable to alkali than its itaconic isomeride.

Equilibration of these acids was carried out at first under the standard conditions, but little or no change occurred. Boiling 60% potash solution, on the other hand, produced considerable secondary change (formation of lactonic acid), but boiling 33% or 25% alkali solution effected a slow interconversion without side reaction. The recovery of equilibrated material was excellent (97—99%) and its analysis, which was readily carried out by the iodometric method, gave the following results :

TABLE II.

Interconversion of the Acids (V) and (VI) with Boiling Aqueous Potash.

Expt. No.	Initial acid.	Concentration of alkali, %.	Equiv. of alkali used.	Time of treatment (hours).	% Change.
16	Itaconic	33	11	66	19
17	,,	25	22	357	27
18	Aticonic	33	11	65	4
19	,,	25	22	370	13
20	,,	25	22	626	21

A special search was made for the corresponding citraconic acid, but the only material volatile in steam was a trace of the itaconic acid. This is therefore volatile in steam at 100° as well as in superheated steam, as reported by Stobbe (Annalen, 1902, **321**, 106). The only evidence of the presence of a third acid in the equilibrated material was obtained in one experiment, where a trace of a crystalline compound, m. p. 156°, apparently isomeric with the other acids, was isolated : from its low melting point, this is regarded as the cis-form of the itaconic rather than as the mesaconic acid.
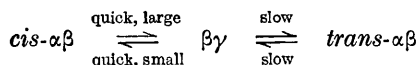
The results in Table II showed that the mobility was so low (less than 0·02 in boiling 25% potash solution) that direct determination of the equilibrium by experiments on the pure isomerides

would be impracticable. The comparable experiments 17 and 19 indicated, however, that at equilibrium there would be an approximate itaconic–aticonic ratio of 3 : 7. A synthetic mixture containing 29% of itaconic acid, equilibrated for 280 hours with boiling 25% potash solution, yielded a product containing 28·4% of itaconic acid, which is accordingly taken to represent the equilibrium in the series.
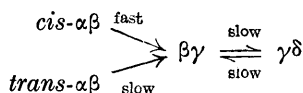
The results obtained by iodometric analysis were confirmed qualitatively by isolation of aticonic acid from the equilibrated itaconic acid, and the reverse.

Discussion.

The study of the tautomerism of the itaconic acids by Fittig (*Annalen*, 1898, **304**, 117, etc.) and in the present work leads to the following general conclusions : I. Systems in which no aticonic form is possible undergo the changes :

$$cis\text{-}\alpha\beta \underset{\text{quick, small}}{\overset{\text{quick, large}}{\rightleftharpoons}} \beta\gamma \underset{\text{slow}}{\overset{\text{slow}}{\rightleftharpoons}} trans\text{-}\alpha\beta$$

The equilibrium between the $\beta\gamma$- and the *trans*-$\alpha\beta$-form is generally on the $\alpha\beta$-side, but it is not certain that the forward and the reverse reaction occur under the same conditions. II. When an alkyl group is substituted for hydrogen attached to the γ-carbon atom, the observed changes are :

$$\begin{array}{c} cis\text{-}\alpha\beta \overset{\text{fast}}{\searrow} \\ \phantom{cis\text{-}\alpha\beta} \searrow \beta\gamma \underset{\text{slow}}{\overset{\text{slow}}{\rightleftharpoons}} \gamma\delta \\ trans\text{-}\alpha\beta \text{slow} \end{array}$$

A complete comparison between these acids and those of the monobasic acid series is not yet possible owing to the absence of quantitative data on such fundamental systems as the *n*-butenoic acids, and a full discussion on this topic must therefore be postponed. Attention may, however, be directed to a few salient points : (i) the extraordinary instability of the $\alpha\beta$-double bond in all citraconic and mesaconic acids in which the itaconic isomeride is stabilised by a γ-substituent, which is difficult of explanation on any theory of prototropic change; (ii) the enormous depression of mobility by the $\alpha\text{-}(CH_2\cdot CO_2^-)$ group in the methylethylitaconic acid series. This is comparable with, but apparently greater than, the low mobilities of various α-alkylated systems studied in these laboratories. It is important to recognise, however, that this effect is not brought about by the $(CH_2\cdot CO_2^-)$ group alone, for Fittig and Petkow (*Annalen*, 1899, **304**, 208) have shown that equilibration of dimethylitaconic acid is moderately fast (compare

Fichter and Probst, *Annalen*, 1910, **372**, 77). Considerable depression of mobility seems to be brought about only when the molecule is already fairly heavily substituted and hence is probably due largely to steric inhibition (Linstead, J., 1929, 2498).* (iii) The equilibria in itaconic–aticonic tautomerism appear to obey the general rules for monobasic acids. For instance, that observed for the γ-methyl-γ-ethyl acids resembles that found for the corresponding acrylic acid without the α-($CH_2 \cdot CO_2^-$) group. Straight chain itaconic acids are stable in the itaconic phase, and the abnormality of *iso*propylitaconic acid, which is apparently stable to boiling alkali solution (Fittig and Burwell, *Annalen*, 1899, **304**, 259), is probably due to the low mobility of the doubly substituted system. The corresponding aticonic acid (which has not yet been examined) should also be stable. (iv) A β-methyl group in a *n*-butenoic acid system is not sufficient to confer appreciable stability on the unstable vinylacetic (βγ-) phase (Found : 100% αβ ; Kon and Linstead, J., 1925, 616). On the other hand, the present work shows that the β-carboxylate ion of itaconic acid gives the βγ-phase a definite measure of stability (16%). This can be interpreted on the basis of the increasing inductive electron-repelling effect of the groups $(H) < CH_3 < CO_2^-$ (Ingold, Shoppee, and Thorpe, J., 1926, 1477). From a study of the addition reactions of the related esters, Ingold, Shoppee, and Thorpe (*loc. cit.* ; compare Hope, J., 1912, **101**, 892) have concluded that the β-carbethoxyl group also has a stabilising effect on the βγ-phase. In this case, however, the tautomeric change, uninfluenced by secondary reactions, has not been studied, and it is not yet possible to accept Shoppee's statement that the itaconic is the " favoured phase " of the system (*loc. cit.*, p. 972).

EXPERIMENTAL.

Molecular weights (*M*) were determined by titration with $N/10$-barium hydroxide ; iodine additions (*J*) were those for 5-minute reactions under the conditions of Linstead and May (J., 1927, 2565).

Citraconic, Mesaconic, and Itaconic Acids.—The acids were prepared and purified by the classical methods (Fittig and Landolt, *Annalen*, 1877, **188**, 72 ; Fittig and Langworthy, *loc. cit.*) with the following modifications to enable reasonable quantities to be prepared quickly.

* In a recent paper (J., 1930, 968) Shoppee justly observes that the removal of the mobile hydrogen in prototropic change will be facilitated by the approach of the " catalytic " ion and it is clear that the original suggestion made by one of us is incorrect and that there will be steric impedance of both the approach of the catalyst and the return of the proton.

For the preparation of mesaconic acid, citraconic acid (30 g.) was dissolved in dry ether (120 c.c.) in a quartz flask fitted with a reflux condenser, and 20 c.c. of chloroform and a few drops of a chloroform solution of bromine were added. The mixture was irradiated by a mercury vapour lamp for 24 hours with occasional addition of more of the bromine solution. The separated solid, after being washed with a little ether (yield, 67%), melted at 201—202°, and at 204° after one recrystallisation from water.

For the preparation of itaconic acid, citraconic acid (70 g.) and water (175 c.c.) were introduced into the porcelain "liner" of a small autoclave, the "liner" being surrounded by a further 500 c.c. of water. The autoclave was heated to an internal temperature of 160° for 8 hours; the porcelain container then held about 500 c.c. of solution. Evaporation of this yielded 32 g. of itaconic acid, m. p. 165° (partial decomp.) after one recrystallisation from water.

Volatilities in Steam.—Citraconic acid (5 g.) in 100 c.c. of water was distilled in steam, the volume of the solution in the distillation flask being kept constant. The distillate (2 litres) was treated with 10 g. of calcium carbonate, evaporated almost to dryness, acidified with 20% sulphuric acid, and extracted for 24 hours in a continuous ether extractor. On removal of the solvent from the dried extract, 3·5 g. of acid were obtained, m. p. 85°. An additional $2\frac{1}{2}$ litres of water carried over 0·9 g. more acid, m. p. 84°, and extraction of the residual solution removed 0·4 g. of acid, m. p. 84°; no itaconic acid was formed. The citraconic acid obtained in these extractions appeared from its consistency and m. p. to be contaminated with a liquid impurity which could not be separated by extraction with sodium bicarbonate solution.

In another experiment 3 g. of pure citraconic acid (m. p. 94°; *M*, 130; calc., 130) were distilled in 5 litres of water and extracted as before; 2·9 g. of material were obtained, m. p. 81° with previous softening (*M*, 152). Trituration of this with light petroleum and draining on a porous tile left almost pure citraconic acid (m. p. 94°; *M*, 134). Too little of the liquid impurity (? methacrylic acid) was obtained for examination.

Itaconic acid (2 g.), distilled in $2\frac{1}{2}$ litres of water, gave on direct extraction of the distillate a trace of oil, and 1·95 g. of unchanged material, m. p. 163°, were extracted from the residue. Distillation of mesaconic acid (2 g.) in 2 litres of water carried over a trace (less than 0·1 g.) of solid acid, melting at 195° after being washed with ether and light petroleum. Extraction of the residue yielded 1·9 g. of mesaconic acid, m. p. 200°.

Equilibrations and Analytical Methods.—10·0 G. of material and

exactly 11 equivalents of 25% aqueous caustic potash, contained in a copper flask under a reflux condenser, were plunged into a bath of boiling brine, maintained at 105° by adjustment of the concentration. In the short-time experiments the duration of heating was taken from the time at which the contents of the flask had reached 100°. Equilibration was stopped by cooling the flask in water, and the alkaline solution was at once acidified in the cold with a slight excess of 50% sulphuric acid and extracted continuously with ether for 24 hours. The extract was dried with calcium chloride, and the ether removed, the last trace in an evacuated desiccator. The weight of the product at this stage was never less than 9·7 g., and the equivalent was usually some 2—3% high. The product was then distilled in steam, sufficient water being used to remove the (estimated) quantity of citraconic acid present (2—9 litres).

The non-volatile portion was exhaustively extracted, and the extract was dried and freed from solvent as before. The mixture of mesaconic and itaconic acids obtained was weighed and its equivalent determined, this giving results 1—2% high. The amount of impurity being therefore very small, the mixture was analysed by the bromometric method (preceding paper). The fraction volatile in steam was extracted exactly as in the experiments with pure citraconic acid. The weight of the isolated product was taken as a measure of the citraconic acid present; its purity will be referred to later. The loss in this series of experiments was some 5%.

In addition to the experiments on the pure acids already given, the accuracy of these methods was checked by analysis of two mixtures of known composition, the results being shown below (Table III). The only appreciable error is in the figure for citraconic acid in the mixture rich in that acid. This is due to the secondary decomposition in the steam distillation to which reference has already been made.

TABLE III.

(*Figures in parentheses represent amounts actually present.*)

Mixture.	Citraconic.	Mesaconic.	Itaconic.	Loss.
1	14 (15)	70 (71)	13 (14)	3
2	72 (77)	13 (12)	10 (11)	5

The detailed results of the analysis of the equilibrated products are in Tables IV and V, which provide the data for the general figures already given (Table I).

Isolation of the Pure Acids from Equilibrated Material.—In experiments 4—7, 10, and 14—15, the mixture of mesaconic and

TABLE IV.

Separation of the Volatile Material.

Expt. No.	Acid used.	Time of treatment (mins.).	Material distilled in steam (g.).	Non-volatile material isolated (g.).	Volatile material isolated (g.).	Loss (g.).
1	C	5	9·53 (135)	1·52 (137)	7·41	0·60
2	,,	7	9·97	2·26 (133)	7·20	0·51
3	,,	14	9·60	3·36 (133)	5·45	0·79
4	,,	30	9·37 (132)	5·16 (131)	4·22	—
5	,,	65	9·54 (134)	6·96 (132)	2·01	0·57
6	,,	120	9·48 (132)	7·70 (131)	1·30	0·48
7	,,	360	9·37 (134)	7·97 (131)	1·02	0·38
8	,,	1440	8·7 (141)	7·3 (135)	1·0	0·4
9	M	7	9·73 (133)	9·23 (131)	0·15	0·35
10	,,	40	9·57 (133)	8·38 (132)	0·96	0·23
11	,,	120	9·78 (136)	8·01 (131)	1·17	0·60
12	I	7	9·46 (134)	7·73 (132)	1·0	0·73
13	,,	20	9·56 (140)	7·83 (133)	1·20	0·53
14	,,	31	9·53 (133)	7·72 (132)	1·61	0·20
15*	C	540	9·22 (134)	4·74 (132)	3·92	0·56

Numbers in parentheses are the values obtained for the molecular weights of the products, the theoretical value for the pure acids being 130.

* This experiment was carried out at 75°.

C = citraconic, M = mesaconic, I = itaconic.

TABLE V.

Composition of the Material Non-volatile in Steam.

Expt. No.	% Addition of bromine.	Composition by the bromine addition method.		Composition by actual isolation of the components.		
		% Mesaconic.	% Itaconic.	% Mesaconic.	% Itaconic.	% Loss.
1	58·8	31	69	——	——	——
2	55·3	42	58	·—	——	——
3	51·8	53	47	·——	——	——
4	47·2	68	32	61	32	7
5	43·7	79	21	75	19	6
6	43·3	80	20	77	19	4
7	43·0	81	19	73	20	7
8	42·2	84	16	——	——	——
9	39·7	92	8	——	——	——
10	41·8	85	15	81	16	3
11	42·6	83	17	——	——	——
12	54·8	43	57	——	——	——
13	43·9	78	22	——	——	——
14	42·8	82	18	76	18	6
15	46·7	69	31	62	32	6

itaconic acids was separated into its constituents. The results obtained strikingly confirm the bromometric figures. The procedure adopted, which was based on that of Fittig and Langworthy (*loc. cit.*), is outlined below.

The material (*ca.* 5 g.) was dissolved in some 20 c.c. of boiling

water and allowed to cool, pure mesaconic acid (m. p. 203°) crystal-lising from all the mixtures in nodules. The mother-liquor was concentrated and further crops of mesaconic acid were removed until separation of the large hard prisms of itaconic acid com-menced. Concentration was then allowed to proceed slowly by evaporation at room temperature; the two acids crystallised side by side and could be separated by hand-picking. The two sub-stances were finally dried and weighed and their purity shown by their m. p.'s. The two acids only came out without conglomeration if this very slow crystallisation was carried out. In such separ-ations it was frequently possible to obtain alternate crops of the two acids. For instance, a solution was allowed to deposit itaconic acid until the first crystals of mesaconic acid appeared; it was then filtered, seeded with mesaconic acid, and the process reversed. The isolation of the itaconic acid was almost quantitative, as bold crystals continued to form until the last trace of solvent had evaporated; whereas the last trace of mesaconic acid did not crystallise well. Hence the figures for mesaconic acid obtained by isolation are lower than those obtained by titration (Table V). No trace of any other substance—such as hydroxy-acid—was isolated in these separations of the non-volatile fraction.

The citraconic acid was isolated from the products volatile in steam either by trituration with light petroleum or by dissolution in a little water, followed by extraction with ether, first in small amount to remove the impurity and then exhaustively to recover the citraconic acid. Two examples are given to illustrate the conversion of both itaconic and mesaconic acids into citraconic acid. In Expt. 11 (from mesaconic acid), 1·17 g. of volatile pro-duct had m. p. 87° and M 149. Trituration with petroleum gave citraconic acid, m. p. and mixed m. p. 93°; M 132. In Expt. 12 (from itaconic acid), 1·0 g. of volatile product (m. p. 87°, M 159), similarly treated, gave citraconic acid, m. p. and mixed m. p. 93°; M, 132.

γ-*Methyl*-γ-*ethyl-itaconic and -aticonic Acids* (V and VI).—The two acids were prepared by the methods already described (Linstead and Mann, J., 1930, 2064).

1·79 G. of the pure itaconic acid (m. p. 186° : M, found 172; calc., 172) were distilled in steam, and the residue and distillate worked up by the methods used for citraconic acid. 2 Litres of water carried over 0·12 g. of the acid, which had m. p. (crude) 176°, raised to 185° after successive washing with light petroleum and ether (mixed m. p. 185°). The residue yielded 1·49 g. of the unchanged acid, m. p. 178°. Similarly treated, the aticonic acid was recovered quantitatively from the non-volatile residue.

B B

Mixtures of the pure acids reacted with iodine as follows :

% Itaconic acid	100	80	60	40	20	0
% Addition	6·4	23·8	41·8	60·4	80·3	98·2

Equilibrations.—(1) Neither acid was appreciably affected on being heated with 11 equivalents of 25% caustic potash solution for 8 hours at 100° or for 24 hours at the boiling point.

(2) The aticonic acid was boiled for several hours with 60% caustic potash solution : the recovered acid had M 183.

(3) In the final series of experiments equilibrations were carried out at the boiling point under reflux in a copper flask.   At the end of the desired time the solution was acidified in the cold with a slight excess of 50% sulphuric acid and kept in ice for 1 hour. The separated solid, mainly sodium sulphate, was extracted with ether for 24 hours in a Soxhlet apparatus, and the solution, after being dried and freed from the solvent, yielded a solid acid (A). The filtrate from the original solid was extracted continuously for 24 hours; the extract, treated in the same way, yielded a solid (B).   The combined weight of A and B was equal to about 98% of the initial material.   To facilitate the subsequent separation of the acids, the products A and B were kept apart, and the equivalent and iodine addition of each taken.   The total composition was then calculated from the proportions and compositions of the two fractions.   The results are given in detail in Table VI and in summary in Table III.   The acids used in the equilibrations were not always completely free from isomeride owing to the waste involved in such complete purification.   The absence of extraneous impurity in the initial material was, however, checked in all cases by determination of the equivalent, and its exact composition found iodometrically.   Percentage conversions relate to actual changes throughout.

A mixture of the two acids (J, 71·1%; itaconic acid 29·0%) was boiled for 280 hours with 22 equivalents of 25% caustic potash solution.   The equilibrated material was isolated as before, products A and B being bulked : 99% was recovered in this way with M, 172; J, 72·3%; whence itaconic acid present = 28·4%.

Conversion of (V) *into* (VI).—Of all the products from the equilibrated itaconic acid, product B, expt. 17, had the highest iodine addition.   3·62 G. of this were treated with anhydrous ether (10 c.c.), which left the crude itaconic acid undissolved.   The soluble portion (1·78 g., m. p. 105—110°) was dissolved in boiling water (10 c.c.).   The cold solution left 0·56 g. of material, m. p. 129°, which on recrystallisation from water yielded crystals of perfect aticonic form but melting 10° low (131°).   Repetition of

TABLE VI.

Action of Boiling Aqueous Caustic Potash on the Acids (V and VI).

Experiment No.		16.	17.	18.	19.	20.
Initial material	% Iodine addition	5·8	8·4	95·4	98·3	98·1
	% Itaconic acid (V)	100	98	4	0	0
	Weight taken (g.)	4·00	10·00	5·00	10·00	10·00
Alkali	Concentration % KOH	33	25	33	25	25
	No. of equivalents.........	11	22	11	22	22
Time of treatment (hours)		66	357	65	370	626
Product A	Weight (g.)	2·52	4·78	3·47	1·50	9·95*
	Equivalent	174	173	173	175	173
	% Iodine addition	9·4	8·0	95·8	90·2	79·8
	% Itaconic acid............	96	98	3	10	21
Product B	Weight (g.)	1·31	5·10	1·48	8·34	—*
	Equivalent	178	181	175	175	—
	% Iodine addition	50·1	54·6	79·8	86·3	—
	% Itaconic acid............	51	46	21	14	—
Total % itaconic acid		81	71	8	13	21
% Conversion		19	27	4	13	21

* In experiment 20 products A and B were bulked.

this process raised the m. p. to 133° and a mixture of equal amounts of this substance and the pure aticonic acid (m. p. 141°) melted at 135°. Further separation was not attempted owing to the small amount of material remaining, which had iodine addition 96·6% (whence percentage of aticonic acid = 98).

Conversion of (VI) *into* (V).—Separation was effected by two methods, the product of experiment 20 being used. A sample of this (4·89 g.) was distilled in steam and the first 2 litres were treated in the manner already given for the examination of the pure itaconic acid. An impure sample of this acid was isolated (0·29 g., m. p. 150—165°), which after being washed with ether and crystallised from water had m. p. and mixed m. p. 183°. Continuation of the steam distillation led to a further 0·54 g. of the acid being isolated from 7 litres of water; m. p. 178° after one crystallisation from water (*M*, 173).

In a confirmatory experiment, the same material (3·97 g.) was washed four times with anhydrous ether in diminishing quantities (about 40 c.c. in all). The residue melted at 182°, and at 185° after one crystallisation from water (mixed m. p. 185°; *M*, 172). The presence of aticonic acid in a mixture considerably increases the solubility of the isomeric acid in ether (compare Fittig, *Annalen*, 1899, **304**, 131). This not only prevents the quantitative application of this method but actually makes it impossible for the itaconic acid to be so isolated from mixtures containing less than about 15% of this acid.

A Third Isomeride (? cis-*Form of* V).—Product B, expt. 19,

was extracted with 25 c.c. of dry ether and the soluble portion was crystallised from water. Characteristic nodules of the aticonic acid separated for some time and when almost all had come out a second compound began to crystallise in sheaves of small needles, which grew side by side with the aticonic nodules. In all, less than 0·1 g. of this was obtained. It was sparingly soluble in water and melted at 156°, with previous softening, but its m. p. was not raised after washing with ether, in contrast to the itaconic acid. A mixture with this acid melted at 152° (M, 169).