XXVI.—*The Symmetrical Dimethylsuccinic Acids.*

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INTRODUCTION.

IN 1869, Wislicenus (*Ber.*, 1869, **2**, 720) described as dimethylsuccinic acid a substance which he had observed among the products of the reduction of iodopropionic acid by means of zinc dust. The substance itself was a syrup, which only partially crystallised on long standing, but it yielded a highly characteristic lead salt, which, on analysis, gave results corresponding with the empirical formula $C_6H_8PbO_4$.

Five years later, Weidel (*Annalen*, 1874, **173**, 109), by the reduction of pyrocinchonic acid, $\begin{array}{c} CH_3 \cdot C \cdot CO \\ | \\ CH_3 \cdot C \cdot CO \end{array} > O$, by means of sodium amalgam, obtained a crystalline acid, melting at 170° , which could be sublimed, for the most part without change, and which he termed "hydropyrocinchonic acid."

In 1878, v. Hardtmuth (*Annalen*, **192**, 142), working under the direction of Wislicenus, studied the action of methylic iodide on the sodium compound of ethylic β -methylacetosuccinate in benzene solution, and on hydrolysing, by means of alcoholic potash, the ethereal salt thus formed, obtained a "dimethylsuccinic acid" melting at 170° . The reactions involved in this process may be thus written

In 1882, v. Roser (*Ber.*, **15**, 2012) obtained "hydropyrocinchonic acid" by the reduction of pyrocinchonic acid by means of hydrogen iodide, and found that it melted at 190° . A very similar result was obtained by Weidel and Brix (*Monatsh.*, 1882, **3**, 612), who, however, used sodium amalgam as the reducing agent; the acid they obtained crystallised in glistening, triclinic needles, melting at 189° .

Three years later, Otto and Beckurts (*Ber.*, 1885, **18**, 825) published the results of a detailed investigation on the reduction of pyrocinchonic acid. When this acid was reduced by hydrogen iodide in sealed tubes at 220° , two acids were obtained, which could easily be separated by fractional crystallisation from water; the more insoluble acid melted at $193\text{--}194^{\circ}$, and seemed to be identical with the acids obtained by v. Roser and Weidel and Brix respectively, whilst the other melted at $118\text{--}120^{\circ}$. Quite different results were obtained when sodium amalgam was used as the reducing agent; in this case, in addition to the acid melting at $193\text{--}194^{\circ}$, there was produced an isomeric acid which melted without decomposition at $240\text{--}241^{\circ}$, whilst the acid melting at $118\text{--}120^{\circ}$ was not to be found among the products of reduction. This last experiment gave results, therefore, quite different from that in which hydrogen iodide was employed as the reducing agent, but, on repeating it, no trace of the acid melting at $240\text{--}241^{\circ}$ could be detected amongst the products, which, on the other hand, contained acids melting at $193\text{--}194^{\circ}$ and $118\text{--}120^{\circ}$.

An examination of the acid melting at $193\text{--}194^{\circ}$ showed that when it was heated to 200° it was transformed into an anhydride melting at $186\text{--}187^{\circ}$, which dissolved in hot water, and yielded, not the original acid, but the acid melting at $240\text{--}241^{\circ}$, which they found might be distilled without decomposition. They concluded, therefore, that these acids stood to one another in the same relationship as do fumaric and maleic acids, and they termed them dimethylsuccinic and isodimethylsuccinic acids respectively.*

They found that when the acid melting at $118\text{--}120^{\circ}$ was heated to 160° , it decomposed with evolution of carbonic anhydride, and concluded that it was identical with the ethylmethylmalonic acid prepared in 1880 by Conrad and Bischoff (*Annalen*, **204**, 143, 162), which melt at 118° .

* Otto and Beckurts published their paper in 1885, two years before Wislicenus put forward his views as to the constitution of fumaric and maleic acids. From the views then held as to the constitution of the last-named acids, we may infer that Otto and Beckurts would have assigned the following constitutions to their

In 1886, Bischoff and Rasch (*Annalen*, **234**, 54) prepared a symmetrical dimethylsuccinic acid synthetically by three methods, which may be briefly described as follows.

1. By the action of methylic iodide on the sodium derivative of ethylic propenyltricarboxylate, according to the equation

The oil formed was hydrolysed by means of alcoholic potash, and the tricarboxylic acid thus obtained was heated at 160° until the evolution of gas had entirely ceased.

2. By hydrolysis of ethylic dimethylacetosuccinate (prepared by the action of ethylic α -bromopropionate on the sodium derivative of ethylic methylacetoacetate) by means of alcoholic potash.
3. By the action of methylic iodide on the disodium derivative of ethylic acetylenetetra-carboxylate, according to the equation

The oil formed was hydrolysed by means of potassium hydroxide, and the tetracarboxylic acid obtained was heated at 170° until the evolution of gas had entirely ceased.

They found that the dimethylsuccinic acid obtained by either of these methods melted at 187°, and that on being heated to its melting point it lost water, and yielded an anhydride melting at 87°.

These results were fully confirmed by Leuckhart (*Ber.*, 1885, **18**, 2344), who prepared the acid synthetically from ethylic methylmalonate and ethylic α -bromopropionate. He found that it melted at 188—189°, and at that temperature was converted into an anhydride melting at 78—81°, which, with hot water, yielded, besides the original acid melting at 189°, an isomeride melting at 121—122°. The last-named acid, although it resembled in some respects, such as crystalline form and solubility, the acid melting at 118—120°, obtained by Otto and Beckurts by the reduction of pyrocinchonic acid, differed from it in that it might be distilled apparently without change. It will be observed that Leuckhart's results were quite incompatible with those of Otto and Beckurts; matters were, however, considerably cleared up in the following year, when Otto and Rössing published a remarkable paper (*Ber.*, 1887, **20**, 2737), which contained an entire refutation of the conclusions arrived at by Otto and Beckurts two years previously. They now found that their dimethylsuccinic acid melting at 193—194° is *not* changed, on heating to 200°, into an

anhydride melting at 186—187°, which with water yields "isodimethylsuccinic acid" melting at 240—241°, but, on the contrary, like Bischoff's dimethylsuccinic acid, it was converted into an anhydride melting at 86—87°, which with water yielded the original acid again. The acid, when treated with acetyl chloride, was converted into a mixture of two anhydrides, one of which melted at 86°, and the other at 38°, the last-named, with water, again yielding the original acid melting at 195°.

Further, they found that the acid melting at 121°, which Otto and Beckurts had obtained by the reduction of pyrocinchonic acid, did not decompose at 180° with evolution of carbonic anhydride, and, therefore, could no longer be considered as ethylmethylmalonic acid; on the contrary, it was converted by acetyl chloride into an anhydride melting at 87°, which with water yielded a mixture of two acids melting at 195° and 121° respectively. They concluded, therefore, that both these acids were dimethylsuccinic acids.

In 1888, Zelinsky (*Ber.*, 1888, **21**, 3160) prepared two symmetrical dimethylsuccinic acids by the hydrolysis of α -dimethylcyanosuccinate (obtained by the action of potassium cyanide on ethylic α -bromopropionate) by means of concentrated hydrochloric acid. One acid melted at 192°, and was almost insoluble in cold water; the other melted at 123—124°, and was fairly soluble in water. Both acids, on distillation, were transformed into the same anhydride, melting at 87°, which dissolved in water yielding the lower melting acid. He proposed the following constitutional formulæ for these acids:—

In 1890, Bischoff and Voit (*Ber.*, 1890, **23**, 639) reinvestigated these acids, their results in the main confirming those of Zelinsky. The two acids melted at 194° (para-acid) and 120° (anti-acid) respectively. At temperatures above 200°, both were converted into the same anhydride melting at 87°; this with water yielded a mixture of the para- and anti-acids. The para-acid, however, when heated with acetyl chloride, was converted into an anhydride melting at 38° (see Otto and Rössing), which with water yielded the para-acid again. On heating the anti-acid with concentrated hydrochloric acid at 180—190°, it was transformed into its isomeride.

In 1893, Crum Brown and Walker (*Annalen*, **274**, 41) prepared the symmetrical dimethylsuccinic acids by the electrolysis of potassium ethylic methylmalonate. They found that the para-acid melted

at 193° , and that its dissociation constant was $K = 0.0208$, whereas the anti-acid melted at $120-121^{\circ}$, and had the dissociation constant $K = 0.0138$.

The results of previous workers are given in tabular form on p. 258.

As the descriptions of the properties of the acids obtained by various experimenters differ so widely, the authors determined to carefully re-investigate the subject, with the results described in this communication.

They have prepared the symmetrical dimethylsuccinic acids in two ways, namely (1), by the hydrolysis of ethylic α -dimethylcyanosuccinate with concentrated hydrochloric acid (Zelinsky's method), and (2) by the action of ethylic α -bromopropionate on the sodium derivative of ethylic methylmalonate, subsequently hydrolysing the product with alcoholic potash, and then heating the tribasic acid thus obtained at 200° until the evolution of carbonic anhydride had entirely ceased (Leuckhart's method). In both cases, the authors obtained a mixture of two symmetrical dimethylsuccinic acids, which were separated by fractional crystallisation from water. The melting points of these acids, especially that of the fumaroid (*trans*-) acid, differed materially from those assigned to them by previous investigators. When pure, the fumaroid (*trans*-) acid melts at 209° , and with acetyl chloride yields an anhydride melting at 43° , which by the action of water is reconverted into the *trans*-acid; it must, therefore, be the anhydride of this acid; further, this anhydride, on prolonged heating with acetic anhydride, is transformed into an isomeric anhydride melting at 88° , which, with water, yields the *cis*-acid.

The maleinoid (*cis*-) acid melts at 129° , and with acetyl chloride yields an anhydride melting at 88° , which with water is reconverted into the original acid, and must, therefore, be the anhydride of the *cis*-acid.

Both acids, when heated for a long time at 210° , or on distillation under atmospheric pressure, are converted into the *cis*-anhydride melting at 88° . Each of the anhydrides, when pure, yields with water only *one* acid (not a mixture of acids as stated by some previous investigators); that melting at 43° yields only the *trans*-acid melting at 209° , whilst that melting at 88° yields the *cis*-acid melting at 129° .

The authors have further shown that the *cis*-acid is almost entirely converted into the *trans*-acid when it is heated with concentrated hydrochloric acid in sealed tubes at 180° ; under similar conditions only a very small part of the *trans*-acid is transformed into the *cis*-modification, by far the greater portion of it being recovered unchanged.

Our results may be represented in tabular form as follows (p. 259).

Date.	Investigators and References.	Acids.	m. p. of acids.	Anhydride formation.	m. p. of anhydride.	Anhydride + water.
1869	Wislicenus (<i>Ber.</i> , 2 , 720)	—	Liquid	—	—	—
1874	Weidel (<i>Annalen</i> , 173 , 109)	"Hydropyrocinnchonic acid" ..	170°	—	—	—
1878	v. Hardtmuth (<i>Annalen</i> , 192 , 142) ..	"Dimethylsuccinic acid"	170°	—	—	—
1882	v. Roser (<i>Ber.</i> , 15 , 2012) ..	"Hydropyrocinnchonic acid" ..	190°	—	—	—
1882	Weidel and Brix (<i>Monatsh.</i> , 3 , 612) ..	"Hydropyrocinnchonic acid" ..	189°	—	—	—
1885	Otto and Beckurts (<i>Ber.</i> , 18 , 825)	"Dimethylsuccinic acid" .. "Isodimethylsuccinic acid" .. "Ethylmethylmalonic acid" ..	193—194° 240—241° 118—120°	Maintained at 200°	186—187°	"Isodimethylsuccinic acid," m. p. = 240—241°.
1885	Leuckhart (<i>Ber.</i> , 18 , 2344)	Dimethylsuccinic acid	188—189°	At 200°	79—81°	Mixture of acids, m. p. 189° and 118—120°.
1887	Otto and Rössing (<i>Ber.</i> , 20 , 2737) ..	Dimethylsuccinic acid	193—194° 121°	{ On heating to 200° With acetyl chloride With acetyl chloride	86—87° 38° 87°	195° acid. Do. Mixture of acids, m. p. 195° and 121°.
1888	Zelinsky (<i>Ber.</i> , 21 , 3160)	α -maleinoid .. β -fumaroid	123° 132°	{ On distillation	87°	Maleinoid acid.
1890	Bischoff and Voit (<i>Ber.</i> , 23 , 639)	Para-..... Anti-.....	192° 120°	{ At 200° Acetyl chloride At 200°	87° 38° 87°	Mixture of para- and anti- acids. Para-acid. Mixture of para- and anti- acids.
1893	Crum Brown and Walker (<i>Annalen</i> , 274 , 41)	Para-..... Anti-.....	193° 120—121°	{ —	—	—

EXPERIMENTAL PART.

PART I.—A. *Preparation of the Symmetrical Dimethylsuccinic acids from Ethylic α-Dimethylcyanosuccinate.*

The ethylic α-dimethylcyanosuccinate used in these experiments was prepared by the action of potassium cyanide on an alcoholic solution of ethylic α-bromopropionate, according to the method described by the authors in a previous paper (Trans., 1895, **67**, 420). The first action of potassium cyanide on ethylic α-bromopropionate consists in a replacement of the bromine by the cyanogen group, resulting in the production of ethylic α-cyanopropionate according to the equation

Subsequently a part of the ethylic α-cyanopropionate thus formed condenses with some of the unchanged ethylic α-bromopropionate, the result being the production of *ethylic αα-dimethylcyanosuccinate*, as follows.

The product, after distilling off the alcohol and extracting with ether in the usual manner, consists of a mixture of unchanged ethylic α-bromopropionate, ethylic α-cyanopropionate, and αα-dimethylcyanosuccinate, which are separated by careful fractionation under reduced pressure (30–40 mm.). The ethylic α-bromopropionate distils over between 77° and 85°, and the ethylic α-cyanopropionate between 103° and 110°, whilst the dark-coloured residue in the distilling flask consists for the most part of ethylic αα-dimethylcyanosuccinate. If the distillation be continued further,

a large quantity of a pale yellow oil passes over between 170° and 200° ; this oil was twice fractionated under a pressure of 80 mm., and the portion distilling between 195° and 200° was employed for the preparation of the symmetrical dimethylsuccinic acids.

Hydrolysis of the Oil.—The oil was mixed with about five or six times its bulk of concentrated hydrochloric acid in a large, round-bottomed flask, and to the mixture glacial acetic acid was added, until the oil just dissolved. The whole was then heated on a sand bath in a flask fitted with a long glass tube, ground into the neck to serve as a reflux condenser; when a sample of the liquid no longer deposited an oil on being diluted with water, it was allowed to cool, when a large crop of white crystals separated, consisting for the most part of ammonium chloride. The liquid was then poured into a large basin, and evaporated nearly to dryness, first over a bare flame, and finally on a water bath; water was added to the residue, and the solution again evaporated down in the water bath, this time completely to dryness. In this way, all the acetic acid and the ethylic acetate formed during the hydrolysis was got rid of. The residue was finally dissolved in hot water, when, on cooling, the solution deposited a greyish-white, crystalline mass of the crude acids; this was separated from the mother liquor by filtration at the pump, thoroughly washed with cold water, redissolved in hot water, boiled with animal charcoal, and filtered while hot. The filtrate, on standing, deposited a crop of white crystals, which, after drying, melted at $207\text{--}208^{\circ}$. After another recrystallisation from hot water, the substance melted at 209° . On concentrating the filtrate on the water bath, a further quantity of an acid was obtained on cooling; this acid, separated from the solution by filtration, and recrystallised, also melted at 209° . The filtrate was repeatedly extracted with pure ether, the ethereal solution dried over calcium chloride, and the ether distilled off. The thick, oily residue, which solidified on standing, was dissolved in hot benzene; the solution on cooling deposited crystals melting between 115° and 125° . These were once more crystallised from hot benzene, but no alteration in the melting point occurred; the acid was then dissolved in hot, concentrated, hydrochloric acid, and on cooling this solution crystals separated melting at $128\text{--}130^{\circ}$; after a second crystallisation from hot, concentrated hydrochloric acid, the substance melted at 129° .

The Acid melting at 209° (Trans-dimethylsuccinic acid).

This acid was analysed, with the following results, which agree well with the empirical formula $\text{C}_6\text{H}_{10}\text{O}_4$.

	Found.		Calculated.
	I.	II.	
Carbon.....	49·21	49·49	49·32
Hydrogen....	7·12	6·73	6·85

Trans-dimethylsuccinic acid is only very sparingly soluble in cold, but readily in boiling water. It is almost insoluble in benzene or chloroform, either hot or cold, but is fairly soluble in alcohol or ether.

Salts of the Acid.—To a neutral solution of the ammonium salt was added

- (a.) *Ferric chloride.* A reddish-brown precipitate of the ferric salt was immediately thrown down.
- (b.) *Copper sulphate.* A greenish-blue and very gelatinous precipitate was formed.
- (c.) *Lead nitrate.* A heavy, crystalline precipitate of the lead salt was produced; this was fairly soluble in hot water, and crystallised out again on cooling.
- (d.) *Silver nitrate.* A white precipitate of the silver salt was formed, fairly soluble in cold water.
- (e.) *Calcium chloride.* When calcium chloride was added to a dilute solution of the ammonium salt, no precipitate was produced either in the cold, or even on boiling for a considerable time. When, however, a fairly strong solution of the ammonium salt was used, the calcium salt was immediately precipitated, even in the cold.

We may here remark that the lead, silver, and calcium salts of the *trans*-acid, and especially the last-named, are decidedly more soluble than the corresponding salts of the *cis*-acid.

The Acid melting at 129° (Cis-dimethylsuccinic acid).

This acid was analysed, with the following results.

	Found.	Calculated for $C_6H_{10}O_4$.
Carbon.....	49·38	49·32
Hydrogen	6·88	6·85

Cis-dimethylsuccinic acid is fairly soluble in cold and readily in warm water, alcohol, or ether, separating rapidly from its aqueous solution when this is saturated with gaseous hydrogen chloride. It is more soluble in warm benzene and chloroform than the isomeric *trans*-acid.

Its salts are very similar to those of the *trans*-acid, but the calcium, lead, and silver salts are much less soluble in water than the corresponding salts of the *trans*-acid.

Separation of the Dimethylsuccinic Acids by means of their Calcium Salts.

The marked difference in the solubilities of the calcium salts of the *cis*- and *trans*-dimethylsuccinic acids affords a very convenient method of separating them, and of obtaining them readily in a state of purity. The method employed by the authors may be briefly described as follows.

Calcium chloride was added to a cold dilute solution of the ammonium salts of the two acids, when, after a short time, a white precipitate of the calcium salt of the *cis*-acid was formed; the whole was then gently warmed, and the precipitate collected with the aid of the pump, washed with a little hot water, and dissolved in hot concentrated hydrochloric acid. On cooling, crystals of the *cis*-acid, melting sharply at 129° , were deposited. The filtrate from the first crude precipitate was then concentrated on the water bath, and the small precipitate which separated during the operation, consisting of a mixture of the calcium salts, removed by filtration. On proceeding further with the concentration, a very bulky precipitate came down; this was separated from the mother-liquor with the aid of the pump and after washing with cold water, was dissolved in hot concentrated hydrochloric acid. On cooling, colourless crystals of the *trans*-acid melting at $204\text{--}209^{\circ}$ were deposited; after recrystallisation from water they melted at 209° .

B.—Preparation of the Symmetrical Dimethylsuccinic acids from Ethylic Methylmalonate and Ethylic α -Bromopropionate.

Forty-four grams of ethylic methylmalonate were mixed with a cold solution of 6 grams of sodium in 75 grams of absolute alcohol contained in a flask, and 45 grams of ethylic α -bromopropionate were carefully added. The mixture at once became hot, and sodium bromide began to separate. On heating the mixture in a water bath in a reflux apparatus for two hours, it became quite neutral; and on pouring the contents of the flask into water, a heavy oil separated. This was extracted with ether, the ethereal solution washed with dilute sodium carbonate solution and with water, dried over calcium chloride, the ether distilled off, and the dark-yellow, oily residue (60 grams) hydrolysed without further purification.

Hydrolysis of the Oil.—The oil was slowly added to about twice its weight of potassium hydroxide dissolved in alcohol, and contained in a large flask; there was a considerable development of heat, so that it was necessary to cool the flask well to prevent loss by frothing; the whole was then heated for six hours in a reflux apparatus on the water bath. A potassium salt soon separated, and after the conclusion of the hydrolysis, water was added to the liquid until this had dissolved,

the solution was poured into an evaporating basin, and concentrated on a water bath until all the alcohol had been driven off. The alkaline liquid was then cooled, carefully acidified with dilute hydrochloric acid, and repeatedly extracted with pure ether; the ethereal solution was dried over calcium chloride, the ether driven off, and the oil which was left heated in an oil bath at 200° until the evolution of carbonic anhydride entirely ceased. The oily residue was then dissolved in hot water, the solution boiled with animal charcoal, and filtered whilst hot; on cooling, the filtrate deposited a mass of white crystals, which were separated from the mother liquor by filtration, and washed well with cold water. On recrystallising these from hot concentrated hydrochloric acid, they melted at 209° ; a second recrystallisation from concentrated hydrochloric acid did not alter the melting point. This acid on analysis yielded the following results.

	Found.		Calculated for $C_6H_{10}O_4$.
	I.	II.	
Carbon.....	49.23	49.55	49.32
Hydrogen.....	6.75	6.92	6.85

and was identical in all its properties with the *trans*-acid melting at the same temperature obtained from ethylic $\alpha\alpha$ -dimethylcyanosuccinate as described in the preceding section.

The filtrate, after removal of the acid melting at 209° was concentrated somewhat, and then repeatedly extracted with pure ether, the ethereal solution dried over calcium chloride, and the ether distilled off; a small quantity of a viscous oil was left, which, on standing, solidified almost entirely. This solid mass was ground up and washed with cold benzene to remove any oily matter, and the residue recrystallised from hot concentrated hydrochloric acid; in this way an acid was obtained melting at 125 — 127° , which, after a second recrystallisation, melted at 129° , and was identical in all its properties with the *cis*-acid melting at 130° obtained from ethylic $\alpha\alpha$ -dimethylcyanosuccinate. This acid on analysis yielded the following results.

	Found.	Calculated.
Carbon	49.30	49.32
Hydrogen	6.67	6.85

The amount of *cis*-dimethylsuccinic acid obtained by the method above described is comparatively small, not more than about one-fourth of the weight of the *trans*-acid formed at the same time.

Behaviour of the Dimethylsuccinic Acids on Prolonged Heating with Concentrated Hydrochloric acid in Sealed Tubes at 180° .

1. About 5 grams of the *trans*-dimethylsuccinic acid (m. p. 209°) were sealed up in a tube with about 40 c.c. of concentrated hydro-

chlorig acid, and heated at 180° for eight hours. On cooling, the crystals which had separated were collected, well washed with water, and dried at 100° ; they melted at $200\text{--}204^{\circ}$, and, after recrystallisation from water, at 208° . The mother liquor was extracted with ether, the ethereal solution dried over calcium chloride, and the ether distilled off, when a very small quantity of an oily substance was left; this partially solidified on long standing, and the solid, after drying on a porous plate, was found to melt at $117\text{--}124^{\circ}$. It probably consisted of the *cis*-acid (m. p. 129°), but the amount was exceedingly small, nearly the whole of the *trans*-acid being recovered unchanged.

2. The *cis*-dimethylsuccinic acid (m. p. 129°) was heated in a tube with concentrated hydrochloric acid under pressure, as described in the previous experiment; the crystals which separated on cooling were collected, washed with water, and dried at 100° . They consisted of crude *trans*-dimethylsuccinic acid and melted between 190° and 200° , and, after recrystallisation from water, at $201\text{--}205^{\circ}$. The mother liquor was extracted with pure ether, and, as in the case of the previous experiment, a very small amount of the unchanged *cis*-acid was obtained.

Thus it is evident that, on heating the *trans*-acid under pressure with concentrated hydrochloric acid at 180° , it is only partially transformed into the *cis*-acid, the greater part of it being unchanged, and that when the *cis*-acid is subjected to the same treatment, it is for the most part converted into the *trans*-modification.

PART II.—THE ANHYDRIDES OF *Cis*- AND *Trans*-DIMETHYLSUCCINIC ACIDS.

A. Behaviour of the Dimethylsuccinic Acids on Prolonged Heating at $210\text{--}215^{\circ}$.

1. One gram of the *trans*-acid (m. p. 209°) was heated in a test-tube immersed in an oil bath, the temperature of which was raised fairly rapidly to about 170° , and afterwards gradually to 210° . At about 205° , the substance began to sublime without melting, and condensed on the upper and cooler portion of the tube in beautiful, asymmetric needles, which, after being spread on a porous plate, melted at $195\text{--}198^{\circ}$. When the temperature of the bath had risen to $210\text{--}211^{\circ}$, the substance melted, and water was given off; the bath was now kept at $210\text{--}215^{\circ}$ for half an hour, when the evolution of steam seemed to have ceased entirely. As the contents of the test-tube solidified on cooling, it was broken, and the solid mass spread on a porous plate; it was found to melt roughly between 65° and 85° . When treated in the cold with a dilute solution of sodium carbonate,

no effervescence could be detected, showing, therefore, that the acid had been completely converted into an anhydride. It was then dissolved in pure ether, and the ether allowed to gradually evaporate, when beautiful, colourless crystals were deposited melting at $84-86^{\circ}$, and identical with the anhydride prepared from the *cis*-acid by treatment with acetyl chloride. It dissolved readily in hot water, and after the solution had been cooled and saturated with gaseous hydrogen chloride, the *cis*-acid separated in crystals melting at $126-128^{\circ}$.

2. One gram of the *cis*-acid was subjected to the same treatment as has been described in the previous experiment; at a temperature rather above 200° , water was readily given off; the crude product solidified on cooling, and then melted between 70° and 80° . When treated with a cold, dilute solution of sodium carbonate, there was no evolution of carbonic anhydride, indicating that the transformation into anhydride was complete. The solid mass, which, after recrystallisation from absolute ether melted at 87° , was dissolved in hot water, the solution cooled, and saturated with gaseous hydrogen chloride, when the *cis*-acid separated in crystals melting at $128-129^{\circ}$.

Both the dimethylsuccinic acids, therefore, when heated at $210-215^{\circ}$, are converted into the *same* anhydride, which must be the anhydride of the *cis*-acid, as it yields this acid when treated with water.

B. Behaviour of the Dimethylsuccinic acids on Distillation at the Ordinary Atmospheric Pressure.

1. Two grams of the *trans*-acid were distilled in a small flask into which a thermometer was inserted; a heavy liquid came over between 230° and 235° , which solidified on cooling. The solid mass melted gradually between 70° and 82° , and when treated in the cold with a dilute solution of sodium carbonate, a small portion dissolved with effervescence, and from this solution a small quantity of an acid melting at about 195° was obtained. The anhydride, after treatment with sodium carbonate, and drying on a porous plate, melted at $83-86^{\circ}$, which was raised to 88° by recrystallisation from absolute ether. This anhydride, with water, yielded the *cis*-acid melting at $127-129^{\circ}$.

2. On distilling the *cis*-acid in the manner described in the previous experiment, a liquid passed over between 230° and 235° , which completely solidified on standing. The solid mass, which melted between 78° and 85° , showed no signs of effervescence when treated in the cold with a dilute solution of sodium carbonate, and, after recrystallisation from absolute ether, melted at 88° . When heated with water, it yielded the original *cis*-acid again.

Thus, on distillation under ordinary pressure, both acids are converted into the *cis*-anhydride; in the case of the *trans*-acid, however, the conversion is incomplete, a portion of the acid distilling over apparently unchanged.

C. Distillation of the Trans-acid under Reduced Pressure.

This experiment was undertaken with a view of ascertaining whether the *trans*-acid on distillation under reduced pressure would yield the same anhydride as it did when distilled under ordinary pressure; it was found, however, that it sublimed very readily under reduced pressure, and apparently for the most part unchanged. The sublimate dissolved very readily in dilute sodium carbonate with effervescence, but it had no constant melting point; a small portion melted at a temperature as low as 40° , but by far the greater part of it showed no signs of melting until the temperature had risen to 190° , when it gradually melted between 190° and 198° . It seems probable, therefore, that when the acid is sublimed under these conditions it is to a small extent converted into an anhydride, although we were unable to isolate a pure anhydride from the sublimate.

D. Behaviour of the Acids on heating with Acetyl Chloride or Acetic Anhydride.

1. About 5 grams of the *trans*-acid were mixed with about 7 c.c. of acetyl chloride, and the whole gently heated in a small reflux apparatus for 10 minutes, until the whole of the acid had just dissolved; it was then placed in a vacuum over solid potash, when the excess of acetyl chloride rapidly volatilised, leaving a yellowish-white crystalline mass, which was then dried on a porous plate in a vacuum. The crude product had no constant melting point, part melted between 30° and 40° , but quite half of it did not melt until the temperature had risen to 160° , indicating that a considerable portion of the original acid had remained unchanged. It was accordingly mixed with more acetyl chloride, and heated gently in a reflux apparatus on a sand bath for half an hour; the product, isolated as described above, now melted sharply at 43° . The substance was then heated for about 20 minutes in a reflux apparatus on a sand bath with acetic anhydride, the excess of acetic anhydride distilled off under reduced pressure, and the liquid residue placed in a vacuum over solid potash, where, after standing several days, it solidified to a pure white mass; this was spread out on a porous plate and left in a vacuum over solid potash, after which it melted very sharply at 43° .

The substance was analysed with the following results.

	Found.	Calculated for $C_6H_8O_3$.
Carbon	55.82	56.25
Hydrogen	6.48	6.25

On dissolving this anhydride in hot water, and cooling the solution, white crystals separated, which, after drying on a porous plate, melted at 208° , and were in all respects identical with *trans*-dimethylsuccinic acid. The substance melting at 43° is, therefore, the anhydride of *trans*-dimethylsuccinic acid.

2. Five grams of the *trans*-acid were mixed with 15 grams of acetic anhydride, the whole heated on the sand bath for three hours in a reflux apparatus, and then fractionally distilled under a pressure of 30 mm.; after the greater part of the acetic anhydride had come over, the temperature rose rapidly to 160° , when the receiver was changed, and the portion distilling over between 160° and 180° collected separately, and placed in a vacuum over solid potash. After the substance had become solid, the crystals were dried on a porous plate in a vacuum, when they melted between 40° and 50° , mostly, however, in the neighbourhood of 43° . A portion of the substance was treated in the cold with a dilute solution of sodium carbonate, but not the slightest effervescence could be detected, showing that no free acid was present. This anhydride was again heated with acetic anhydride for three hours, and the treatment described above repeated. Finally we obtained the *cis*-anhydride melting at 88° , which with water yielded the *cis*-acid melting at 129° .

From this experiment, it seemed probable that the *trans*-acid, when heated with acetic anhydride, yields first of all its own anhydride (m. p. = 43°), but that on prolonged heating with acetic anhydride this is converted into the *cis*-anhydride melting at 88° . This conclusion was confirmed as follows: A small portion of the *trans*-anhydride melting at 43° , obtained in D 1, was heated for several hours with acetic anhydride in a reflux apparatus, the excess of acetic anhydride distilled off under reduced pressure, and the residual liquid placed in a vacuum over solid potash. After several days, the liquid deposited crystals, which when dried in a vacuum on a porous plate, were found to melt at 87 – 88° , and with water yielded the *cis*-acid.

Thus the *trans*-anhydride, on prolonged heating with acetic anhydride, is converted into the *cis*-anhydride.

3. Five grams of the *cis*-acid were heated with acetic anhydride for three hours on a sand bath in a reflux apparatus, the excess of acetic anhydride distilled off under reduced pressure, and the residual liquid placed in a vacuum over solid potash. On long standing, the liquid crystallised, and the crystals, after drying on a porous plate, melted at 87° , and on being dissolved in hot water yielded the *cis*-acid melting at 128 – 129° .

The *cis*-anhydride (m. p. 88°) was analysed with the following results.

	Found.	Calculated for $C_6H_8O_3$.
Carbon	55.99	56.25
Hydrogen	6.60	6.25

4. The *cis*-acid was dissolved in a slight excess of acetyl chloride, the solution gently warmed on the sand bath in a reflux apparatus for 20 minutes, and placed over solid potash in a desiccator, which was then exhausted; the acetyl chloride was thus rapidly volatilised, and the residue crystallised on standing. The crystals, after drying in a vacuum on a porous plate, were found to consist of the *cis*-anhydride melting at 88° .

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