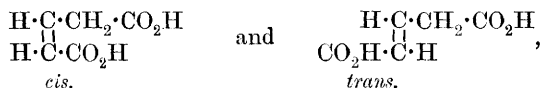


# XLIV.—*Glutaconic Acid and the Conversion of Glutaric Acid into Trimethylenedicarboxylic Acid.*

By WILLIAM HENRY PERKIN, jun., and GEORGE TATTERSALL, B.Sc.

GLUTACONIC ACID has, so far, only been obtained in one modification, although stereochemical theory indicates that the two modifications



corresponding to maleic and fumaric acids, should exist.

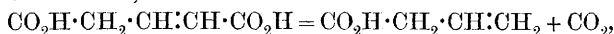
It has been shown by W. H. Perkin, jun., and Alice E. Smith (Trans., 1903, **83**, 8, 771; 1904, **85**, 155) that *aa*-dimethylglutaconic acid,  $\text{CO}_2\text{H} \cdot \text{CMe}_2 \cdot \text{CH} : \text{CH} \cdot \text{CO}_2\text{H}$ , and *aaa*<sub>1</sub>-trimethylglutaconic acid,  $\text{CO}_2\text{H} \cdot \text{CMe}_2 \cdot \text{CH} : \text{CMe} \cdot \text{CO}_2\text{H}$ , both occur in *cis*- and *trans*-modifications, and this fact makes it all the more remarkable that the parent substance—glutaconic acid itself—is only known in one form.

Glutaconic acid melts at 134°, and when heated with acetyl chloride yields an anhydride which melts at 87° and was first prepared by Buchner (*Ber.*, 1890, **23**, 706). In investigating this anhydride, the authors find that it may be distilled without decomposition under

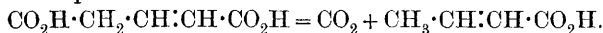
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reduced pressure, and that, as Buchner has stated, it yields, on hydrolysis, the glutaconic acid from which it was prepared. It is therefore certain that the only known modification of glutaconic acid is the *cis*-modification, a view which has already been put forward by Buchner. A large number of experiments were instituted by the authors in the hope of being able to isolate the corresponding *trans*-modification of glutaconic acid, but without success. Several new and interesting facts were, however, brought to light, which may be briefly stated as follows.

When glutaconic acid is distilled, it decomposes into vinylacetic acid and carbon dioxide,



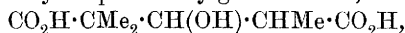
but when heated with water in a sealed tube at  $180^\circ$  the decomposition takes place in another direction and crotonic acid results,



Glutaconic acid yields a characteristic anilic acid (m. p.  $132^\circ$ ) and is readily acted on by bromine with formation of  $\alpha\beta$ -dibromoglutaric acid,  $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{CHBr}\cdot\text{CHBr}\cdot\text{CO}_2\text{H}$  (m. p.  $154$ – $155^\circ$ ).

A series of experiments was next made on the elimination of hydrogen haloids from halogen substitution products of glutaric acid, in the hope that by one, at least, of the methods employed the *trans*-modification of glutaconic acid might be formed.

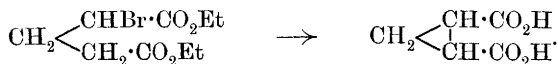
$\beta$ -Hydroxyglutaric acid,  $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , was prepared by the reduction of acetonedicarboxylic acid (Pechmann and Jenisch, *Ber.*, 1891, **24**, 3250), and then converted into ethyl  $\beta$ -chloroglutarate,  $\text{CO}_2\text{Et}\cdot\text{CH}_2\cdot\text{CHCl}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ , by the action of phosphorus pentachloride and then of alcohol. This ester, when treated with diethylaniline and subsequently hydrolysed, yielded *cis*-glutaconic acid. This result is remarkable because, under exactly the same conditions,  $\beta$ -hydroxy-*aaa*<sub>1</sub>-trimethylglutaric acid,



is converted into *trans*-*aaa*<sub>1</sub>-trimethylglutaconic acid (Perkin and Smith, *Trans.*, 1903, **83**, 777).

An experiment was also made in which  $\beta$ -hydroxyglutaric acid was subjected to distillation, but the distillate was found to consist of a mixture of *cis*-glutaconic acid and its anhydride.

Ethyl  $\alpha$ -bromoglutarate was then prepared from glutaric acid in the usual manner and digested, in one experiment, with alcoholic potash, and in another with diethylaniline, and in both cases the product was found to be *trans*-trimethylenedicarboxylic acid :



This remarkable formation of a trimethylene derivative had previously

been observed by Bowtell and Perkin (Proc., 1899, 15, 241), and the experiments described in the present paper entirely confirm the results obtained by these authors. [View Online](#)

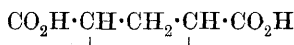
Lastly, the ethyl  $\alpha$ -bromoglutarate just mentioned was converted into ethyl  $\alpha$ -iodoglutarate by digesting in alcoholic solution with potassium iodide, and afterwards hydrolysed by means of alcoholic potash, but in this case also the product obtained was *trans*-trimethylenedicarboxylic acid.

The series of experiments just described, together with those carried out by Miss Smith and one of the authors, make it appear probable that the formula usually assigned to glutaconic acid, namely,



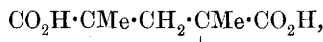
does not always correctly represent the constitution of this acid.

The general behaviour of glutaconic acid seems to indicate that its molecule is symmetrical, and the expression



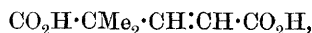
seems to explain, in a more satisfactory manner, many of the remarkable properties of the acid. Such an expression may be considered as a tautomeric modification of the old formula, and therefore capable of being converted into the latter during the course of certain reactions. The new formula may possibly offer an explanation of the probable existence of only one modification of glutaconic acid, since a substance of this constitution would hardly exist in *cis*- and *trans*-modifications, at all events, of the kind met with in the case of fumaric and maleic acids.

As further evidence in favour of the new formula may be mentioned the fact, recently proved by Dr. J.F. Thorpe, that the positions  $\alpha$  and  $\alpha_1$  ( $\alpha$  and  $\gamma$ ) in glutaconic acid are identical, whereas this could hardly be the case if the acid had the constitution  $\text{CO}_2\text{H}\cdot\overset{\alpha}{\text{CH}_2}\cdot\text{CH}\cdot\overset{\alpha_1}{\text{CH}}\cdot\text{CO}_2\text{H}$ . Another interesting observation is the fact that  $\alpha\alpha_1$ -dimethylglutaconic acid, which according to the new formula would be represented thus:



exists, like glutaconic acid itself, apparently in one modification only (compare Reformatsky, *Chem. Centr.*, 1898, ii, 886).

As soon, however, as two methyl groups become attached to one  $\alpha$ -carbon atom, as in the case of the dimethylglutaconic acid,



and the trimethylglutaconic acid,  $\text{CO}_2\text{H}\cdot\text{CMe}_2\cdot\text{CH}\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$ , the

substances become derivatives of the old formula of [glutaconic acid](#),<sup>View Online</sup> and at once, just as in the case of fumaric and maleic acids, *cis-trans*-isomerism is observed.

A further discussion of the constitution of glutaconic acid will appear in a paper by Dr. Thorpe, which is shortly to be published.

## EXPERIMENTAL.

### *Glutaconic Acid, its Anhydride and Decomposition Products.*

The glutaconic acid employed in these experiments was prepared by the method of Conrad and Guthzeit (*Ber.*, 1882, **15**, 2841), and, after several crystallisations from water, it melted at 134°.

When glutaconic acid is heated in a retort under the ordinary pressure, it melts and gradually darkens in colour; carbon dioxide and water are eliminated, a small quantity of a pungent-smelling acid liquid distils over, and a considerable amount of a carbonaceous mass remains in the retort. The distillate from a number of operations was dissolved in a little ether, dried over calcium chloride, the ether evaporated and the residue twice fractionated, when a mobile liquid was obtained which distilled at about 165° and gave the following results on analysis:

0.1568 gave 0.3196 CO<sub>2</sub> and 0.1022 H<sub>2</sub>O. C = 55.6; H = 7.2.

C<sub>4</sub>H<sub>6</sub>O<sub>2</sub> requires C = 55.8; H = 7.0 per cent.

This acid is obviously produced by the elimination of carbon dioxide from glutaconic acid and might therefore be either crotonic acid, *iso*-crotonic acid, or vinylacetic acid. When cooled in a freezing mixture, it showed no signs of crystallising, and, since the crotonic acids readily solidify under these conditions, it is probably vinylacetic acid.

When glutaconic acid is distilled under a 12 mm. pressure, an oil passes over between 150—210° and crystallises on cooling. The crystals consist of glutaconic anhydride mixed with a considerable quantity of the unchanged acid.

An experiment was next made on the action of dilute hydrochloric acid on glutaconic acid. The pure acid was dissolved in 5 per cent. hydrochloric acid solution and heated in a sealed tube at 180° for one hour. On opening the tube, a quantity of gas escaped which proved to be carbon dioxide. The liquid was extracted with ether, the ethereal solution dried and evaporated, and the residue distilled, when an oil passed over at 170—180° which, on cooling, partially solidified. The oil was removed by contact with porous porcelain and the residue crystallised from light petroleum, when needle-shaped crystals were obtained which melted at 71—72° and gave the following results on analysis:

0.0838 gave 0.1721 CO<sub>2</sub> and 0.0520 H<sub>2</sub>O. C = 56.0; H = 6.8. [View Online](#)

C<sub>4</sub>H<sub>6</sub>O<sub>2</sub> requires C = 55.8; H = 7.0 per cent.

The properties of this acid leave no doubt that it was crotonic acid, CH<sub>3</sub>·CH:CH·CO<sub>2</sub>H.

In order to investigate further the properties of glutaconic anhydride, a considerable quantity of this substance was prepared by the method recommended by Buchner (*Ber.*, 1890, 23, 706), namely, by treating the acid with acetyl chloride. As observed by Buchner, this anhydride, when heated under the ordinary pressure, decomposes at about 130°; but the authors find that, when heated under 15 mm. pressure, it distils for the most part unchanged at 152–153°. The oily distillate solidifies quickly to a mass of needles which, after draining on porous porcelain and recrystallising from ether, melt sharply at 87°.

When the solution of the anhydride (1 gram) in dry ether (150 c.c.) is mixed with aniline (1 gram), a white solid separates, but, on boiling, this again passes into solution. If the bulk of the ether is distilled off and the residue allowed to stand, colourless prisms separate, which, after recrystallisation from ether, melt at 128–132° and consist of *glutaconanilic acid*.

0.2120 gave 12.7 c.c. of nitrogen at 18° and 755 mm. N = 7.2.

C<sub>11</sub>H<sub>11</sub>O<sub>3</sub>N requires N = 6.9 per cent.

### *Experiments with Glutaric Acid and its Derivatives.*

The first series of experiments was made with β-hydroxyglutaric acid, CO<sub>2</sub>H·CH<sub>2</sub>·CH(OH)·CH<sub>2</sub>·CO<sub>2</sub>H, which was prepared in quantity by the reduction of acetonedicarboxylic acid (Pechmann and Jenisch, *Ber.*, 1891, 24, 3250). It was, however, found unnecessary to carry out the tedious purification by means of the copper salt which these chemists recommend. The product of the reduction is acidified with hydrochloric acid, evaporated to dryness, and extracted with ether in a large Soxhlet apparatus. The ethereal solution, after drying over calcium chloride and evaporating to a small bulk, slowly deposits crystals of pure β-hydroxyglutaric acid. When this hydroxy-acid is distilled under 18 mm. pressure, water is eliminated and the boiling point rises continuously to about 210°. The distillate, which quickly solidifies, consists of a mixture of glutaconic acid and glutaconic anhydride, and not of the acid alone as stated by Pechmann and Jenisch (*loc. cit.*).

Ethyl β-chloroglutarate was prepared from the β-hydroxy-acid in the following way. The hydroxy-acid (6 grams) was left in contact with phosphorus pentachloride (25 grams) in the cold until all action had ceased; the product was then heated for a short time on the water-

bath and poured into 200 c.c. of absolute alcohol. The [alcoholic solution](#) was mixed with water, extracted with ether, the ethereal solution washed well with dilute sodium carbonate, dried over calcium chloride, evaporated, and the residue left over sulphuric acid in a vacuum desiccator for two days.

The analysis gave numbers agreeing only approximately with those required.

0.2525 gave 0.1430 AgCl. Cl = 14.0.

$C_9H_{15}O_4Cl$  requires Cl = 16.0 per cent.

The ester thus obtained was heated with about twice its volume of freshly distilled diethylaniline at 150° for 15 minutes; the dark product was poured into dilute hydrochloric acid, extracted with ether, the ethereal solution washed with dilute acid, dried over calcium chloride, and evaporated. The residual oil was hydrolysed with methyl-alcoholic potash and, after removal of the alcohol by the addition of water and evaporation, the residue was acidified and extracted with ether. The solid mass obtained on distilling off the ether was recrystallised from water, when nearly colourless crystals were obtained which melted at 130–132° and consisted of *cis*-glutaconic acid.

The last series of experiments made was with the  $\alpha$ -halogen substitution products of glutaric acid. Ethyl  $\alpha$ -bromoglutarate,



was prepared by heating glutaric acid (5 grams) first with phosphorus pentachloride (16 grams) on the water-bath and then with bromine (6.5 grams) in a sealed tube for one hour. The product was poured into excess of alcohol, and, after several hours, water was added and the bromo-ester extracted with ether. The ethereal solution was well washed with dilute sodium carbonate, and evaporated, when ethyl  $\alpha$ -bromoglutarate was obtained as an oil which, after standing for some days over sulphuric acid in a vacuum desiccator, was analysed:

0.1803 gave 0.1256 AgBr. Br = 29.4.

$C_9H_{15}O_4Br$  requires Br = 30.0 per cent.

The ethyl  $\alpha$ -bromoglutarate thus obtained was mixed with a large excess of a strong solution of methyl-alcoholic potash and heated to boiling for one hour, during which operation a quantity of potassium bromide separated. After adding water and evaporating almost to dryness, the product was acidified with hydrochloric acid and extracted several times with ether. The ethereal solution was dried over calcium chloride and evaporated, when a yellow, oily residue was obtained, which soon deposited a quantity of crystals. The crystals were freed from adhering oil by spreading on porous porcelain, and then crystal-

lised from water, from which the acid separated in prisms melting at 173—174°. [View Online](#)

0.1623 gave 0.2755 CO<sub>2</sub> and 0.0672 H<sub>2</sub>O. C = 46.3; H = 4.6.

C<sub>5</sub>H<sub>6</sub>O<sub>4</sub> requires C = 46.1; H = 4.6 per cent.

Since this acid was found to be quite stable towards permanganate, it could not be unsaturated, and the only other alternative was that it was a trimethylene derivative. Careful comparison showed that it was *trans*-trimethylenedicarboxylic acid (1, 2), a result which confirms the previous experiments of Bowtell and Perkin (Proc., 1899, 15, 241). The action of diethylaniline on ethyl  $\alpha$ -bromoglutarate was also investigated, and an ester was obtained which, on hydrolysis, again yielded *trans*-trimethylenedicarboxylic acid.

Lastly, ethyl  $\alpha$ -iodoglutarate was prepared, and its behaviour on hydrolysis investigated. Ethyl  $\alpha$ -bromoglutarate (10 grams) was digested in alcoholic solution with finely powdered potassium iodide (7 grams) for four hours, during which operation much potassium bromide separated. After diluting with water, the product was extracted with ether, the ethereal solution washed with sodium hydrogen sulphite until free from iodine, dried over calcium chloride, and evaporated. After remaining for some hours over sulphuric acid in an exhausted desiccator, the following results were obtained on analysis:

0.1896 gave 0.1349 AgI. I = 38.7.

C<sub>9</sub>H<sub>15</sub>O<sub>4</sub>I requires I = 40.4 per cent.

This crude iodo-ester was treated with alcoholic potash in the manner described in the case of the corresponding bromo-ester, with the result that *trans*-trimethylenedicarboxylic acid was again obtained as the principal product of the reaction.

In conclusion, the authors desire to express their thanks to the Research Fund Committee of the Chemical Society for a grant, out of which much of the expense of this research was defrayed.

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