LXXX.—*Homologues of Butanetetracarboxylic acid and of Adipic acid.**

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INTRODUCTION.

WHEN ethylene dibromide is treated with the monosodium derivative of ethylic malonate, the chief product is ethylic 1:1-trimethylene-dicarboxylate (Perkin, Trans., 1887, 51, 1).

but, at the same time, an oil of high boiling-point is formed, which, however, constitutes only about 3 per cent. of the whole; this, on investigation, was found to be ethylic butanetetracarboxylate, and its formation may be represented by the equation—

The fact that this substance is produced in such small quantities made its further investigation a matter of very great difficulty; more recently, however, Professor W. H. Perkin, jun., has found that the substitution of ethylenic chloride for the bromide greatly increases the yield of ethylic butanetetracarboxylate. The method

* Part of a thesis accepted for the degree of Doctor of Science of the University of London.

which is now adopted for the preparation of this substance is described in a paper published in this Journal (this vol., 578).

Ethylic butanetetracarboxylate, in constitution and properties, is very closely allied to the ethereal salts of ethane-, propane-, and pentane-tetracarboxylic acids, all of which have been investigated in detail.

These ethereal salts interact with sodium ethylate, forming disodium derivatives, the sodium displacing the hydrogen atoms of the two CH groups, and giving compounds, which, if X denote the group COOEt, may be represented thus—

When these sodium derivatives are treated with alkylic haloïds disubstitution derivatives are formed of the general formulæ—

in which R represents an alkylic group, the action taking place readily, except in the case of the disodium derivative of ethylic ethane-tetracarboxylate, when it is necessary to heat the mixture at 150° (Guthzeit and Dressel, *Annalen*, **256**, 181; Perkin, *Trans.*, 1891, **59**, 818; Baeyer and Perkin, *Ber.*, **17**, 449).

On hydrolysis, these ethereal salts yield the corresponding tetracarboxylic acids, which lose 2 mols. of carbonic anhydride when heated at about 200°, and are converted into derivatives of succinic, glutaric and pimelic acids, of the general formulæ—

where Y represents the group COOH, just as ethylic ethane-, propane-, and pentane-tetracarboxylates, under similar circumstances, are converted into succinic, glutaric and pimelic acids respectively.

It has already been shown by Perkin (*loc. cit.*) that ethylic butanetetracarboxylate is capable of forming a disodium derivative $(\text{COOEt})_2\text{CNa} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CNa}(\text{COOEt})_2$, and that this disodium derivative is converted by iodine into the ethereal salt of tetramethylenetetracarboxylic acid, thus—

but no further experiments could be instituted at that time with the disodium derivative, owing to the difficulty of obtaining sufficient of the ethereal salt. When, however, the method of preparation had been so improved as to make it possible to continue, in a satisfactory

manner, the investigation of the substance, it was thought that interesting results would be obtained by studying the action of alkylic haloids on the disodium derivative.

In carrying out this investigation, it was found that the disodium derivative of ethylic butanetetracarboxylate is readily acted on by alkylic iodides or chlorides, forming $\alpha\alpha$ -dialkyl-substituted butanetetracarboxylic acid derivatives, thus—

The action takes place as soon as the substances are brought together, generally with considerable development of heat.

On the other hand, it has not been found possible to prepare monalkylic derivatives of butanetetracarboxylic acid by the action on ethylic butanetetracarboxylate of 1 mol. of sodium ethylate and 1 mol. of an alkylic haloid. On attempting to prepare ethylic monethylbutanetetracarboxylate in this way, the product was found to consist of ethylic diethylbutanetetracarboxylate, one half of the ethylic butanetetracarboxylate being recovered as such. In explanation of this remarkable action, one must either suppose that ethylic butanetetracarboxylate is incapable of forming a monosodium derivative under such conditions, or that the decomposition of the monosodium derivative takes place thus—

Similarly, ethylic propanetetracarboxylate (Guthzeit and Dressel, *Annalen*, **256**, 180, 188), and ethylic pentanetetracarboxylate (Perkin, *Trans.*, 1891, **59**, 847), when treated with 1 mol. of sodium ethylate and an alkylic haloid, yield, instead of a monalkylic derivative, a mixture of the dialkyl derivative with unchanged ethereal salt.

In the course of this investigation, a detailed study has been made of the dimethyl, diethyl, dicetyl, and dibenzyl derivatives of ethylic butanetetracarboxylate. They are all solids, and crystallise with considerable facility.

On hydrolysis, these ethereal salts yield the corresponding quadricarboxylic acids, which possess some very remarkable properties;

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for, although they contain four carboxyl groups, they do not in all cases behave as quadribasic acids. When their basicity is determined by titration with standard solution of potassium hydrate, some of them act as bibasic acids; notably is this the case with dibenzylbutanetetracarboxylic acid, the result being the same whether phenolphthalein or litmus is used as the indicator. In this connection, it is to be noted that the silver and calcium salts of dibenzylbutanetetracarboxylic acid, which were obtained, were found to have the formulæ $C_{22}H_{20}O_8Ag_2$ and $C_{22}H_{20}O_8Ca + 2H_2O$ respectively. On the other hand, dimethyl-, diethyl-, and dicetyl-butane-tetracarboxylic acids, on being titrated with potassium hydrate, give different results, according as phenolphthalein or litmus is employed as indicator. They behave as quadribasic acids when phenolphthalein is used. If, however, one or two drops of litmus solution be added to the solution of these acids in potassium hydroxide, which has been rendered neutral to phenolphthalein by hydrochloric acid, a distinctly blue coloration is produced. On adding more hydrochloric acid, the blue coloration changes gradually to red, and the solution appears to become neutral to litmus only when sufficient hydrochloric acid is added to neutralise one half of the potassium hydroxide, which was equivalent, as shown by phenolphthalein, to the tetracarboxylic acid present. While the salts of dimethyl- and diethyl-butane-tetracarboxylic acid were quadribasic, those prepared in the same way from dicetylbutane-tetracarboxylic acid, like those of dibenzylbutane-tetracarboxylic acid, were found to be bibasic.*

* As regards the action of indicators, it has been shown that the quadribasic potassium salts of dimethyl-, diethyl-, and dicetyl-butane-tetracarboxylic acid are neutral to phenolphthalein but alkaline to litmus, and that, on titrating these acids, when using litmus as the indicator, the points of neutralisation are found to be very indefinite. Dibenzylbutane-tetracarboxylic acid, on the other hand, acts as a bibasic acid, both towards litmus and phenolphthalein. To illustrate further the difference in behaviour of indicators, reference may be made to a systematic investigation of the use of litmus, methyl-orange, and phenolphthalein as indicators, which was carried out by Smith in 1883 (*Chem. News*, 1883, **47**, 136). The following table is compiled from his results.

	Oxalic.	Acetic.	Tartaric.	Citric.
Methyl-orange..	low results	very low results	very low results	very low results
Litmus	sharp	indefinite	indefinite	indefinite
Phenolphthalein	sharp	sharp	sharp	sharp

Engel (*Compt. rend.*, 1886, **102**, 262), too, has shown that when a solution of phosphoric acid is tritrated, it appears to be monobasic if methyl-orange is used as the indicator, but bibasic with phenolphthalein, and tritasic with Poirier's soluble

When heated at 200—210°, the disubstituted butanetetracarboxylic acids readily lose 2 mols. of carbonic anhydride, yielding disubstituted adipic acids.

The study of these disubstituted adipic acids is especially interesting in view of the recent work of Bischoff, Auwers and Victor Meyer, Zelinsky, Perkin, and others, on the isomerism of α -disubstituted acids in the succinic, glutaric, and pimelic series.

The symmetrical disubstituted succinic acids (Leuchart, *Ber.*, **18**, 2348; Zelinsky, *Ber.*, **21**, 3170; Bischoff and Voit, *Ber.*, **20**, 2988; Hell and Rothberg, *Ber.*, **22**, 66; Bischoff and Voit, *Ber.*, **22**, 389; Bischoff and Hjelt, *Ber.*, **21**, 2089, 2097, 2102; Bischoff, *Ber.*, **20**, 2968; Hjelt, *Ber.*, **20**, 3078; Bischoff and Mintz, *Ber.*, **23**, 650; Butchichin and Zelinsky, *Abstr.*, 1889, 377; 1890, 740) are found to exist in two well marked isomeric forms; for instance, two dimethylsuccinic acids are known, melting at 123—124° and 192°, and two diethylsuccinic acids, melting at 129° and 192°. The isomerism of the disubstituted glutaric acids is, apparently, not so pronounced as that of the disubstituted succinic acids; of the dialkyl-glutaric acids (Zelinsky, *Ber.*, **22**, 2823; Bischoff, *Ber.*, **23**, 1465; Bischoff and Mintz, *Ber.*, **23**, 649; Auwers and Köbner, *Ber.*, **24**, 1933; Guthzeit and Dressel, *Annalen*, **255**, 171), the dimethyl derivatives alone have been separated into two distinct modifications, melting at 102—104° and 128° respectively. A number of disubstituted pimelic acids (Perkin and Prentice, *Trans.*, 1891, **59**, 818) have been prepared, but in no case could a separation into two isomerides be satisfactorily accomplished; it was, however, frequently noticed that the melting-points of the acids were not so sharp as could be desired, and there is reason to believe that these acids also occur in two isomeric forms, which are so similar in properties that separation is a matter of great difficulty.

Considerable interest, therefore, attaches to the question of isomerism in the disubstituted adipic acids, as these are intermediate between the glutaric and pimelic acids. It has been found in the course of the present research that these disubstituted adipic acids invariably exist in two modifications, which usually differ from one another in a

blue. He also showed that boric acid is neutral to methyl-orange, feebly acid to litmus or phenolphthaleïn, and acid to soluble blue. From these instances, it appears that litmus is liable to give lower results than phenolphthaleïn, and in the case of litmus the final colour change is usually very indefinite.

It also is evident that any knowledge of the basicity of an acid obtained by titration is only relative to the nature of the indicator employed, and, further, when a polybasic acid has been only partially neutralised, its acid function may be enfeebled altogether out of proportion to the amount of base which has been added to it. This raises the wider question of the basicity of polybasic acids, and of their affinity as a function of the affinities of the groups which they contain. (See "Note on the Affinities of Polybasic Acids," this vol., p. 1024.)

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very marked manner in melting-point, solubility, and other physical properties.

For instance, the dimethyladipic acids melt at 70—72° and 142°, the diethyl at 51—53° and 136°, the dibenzyl at 152° and 211—213°. It is remarkable that the isomerism of these disubstituted acids is as pronounced in the adipic series as in the succinic, whilst in the intermediate glutaric series it is much less noticeable. Of these derivatives of adipic acid, the dimethyl alone have previously been obtained (Zelinsky, *Ber.*, **24**, 3997), through the hydrolysis of ethylic dicyanodimethyladipate with sulphuric acid, as represented by the equation—

It is a well-known fact that whilst oxalic acid, or malonic acid and its alkylic derivatives, do not form internal anhydrides, the formation of an anhydride occurs readily in the case of succinic acid, and it is exceedingly interesting that the introduction of alkylic groups much increases the tendency to form anhydrides (Bischoff and Mintz, *Ber.*, **23**, 620 and 656; Auwers and Jackson, *Ber.*, **23**, 1614); for instance, dimethylsuccinic acid yields an anhydride much more readily than succinic acid, and again anhydride formation takes place more readily in the alkylic derivatives of glutaric acid than in the case of the acid itself. Now adipic acid does not form an anhydride, but the introduction of methyl or other groups appears to increase the tendency to form an anhydride, and Manasse and Rupe (*Ber.*, **27**, 1818; 1894) have very recently succeeded in obtaining the anhydride of β -methyladipic acid; it is noteworthy that it is very unstable, and reverts to the acid on long exposure to the air. The disubstituted adipic acids, described in the following pages, when heated with acetyl chloride in sealed tubes, in no case gave an anhydride; in view, however, of the work of Manasse and Rupe (*loc. cit.*), it is possible that sufficient precautions were not taken to prevent the access of moisture from the air during the working up of the product; further experiments are in progress to decide this point.

Whilst, however, no anhydride was formed on heating the disubstituted adipic acids in sealed tubes with acetyl chloride, it was found that, whether the higher-melting or lower-melting modification was employed, a partial conversion of the one into the other was effected, the product consisting of a mixture of the two. Similarly, when the symmetrical disubstituted succinic acids (Bischoff and

Mintz, *Ber.*, **23**, 656) are heated in sealed tubes at 200°, in each case a mixture of the two modifications of the acid is formed. A similar conversion can be effected in the case of the dimethylglutaric acids (Zelinsky and Besredka, *Ber.*, **24**, 465; Auwers and Köbner, *Ber.*, **24**, 1933).

It remains to refer to the theories which have been advanced to account for the two modifications of these symmetrical *az*-disubstituted dicarboxylic acids. From the close analogy between the constitution of a symmetrical *az*-dialkylsuccinic acid and that of a tartaric acid, each containing a pair of asymmetric carbon atoms, according to one view (Bischoff and Walden, *Ber.*, **22**, 1819), it has been held that any two isomeric symmetrical disubstituted succinic acids correspond to the two inactive tartaric acids, the one being inactive through intramolecular compensation of right- and left-handed groups, whilst the other consists of a mixture of equal quantities of the active right- and left-handed acids. If this is so, it should be possible to resolve one or other of the two substituted succinic acids into two active constituents. The chief objection which this theory has to meet is that hitherto in no case has this resolution into active forms been accomplished, although repeated attempts have been made in the case of the substituted succinic acids (Bischoff and Walden, *loc. cit.*).

As a result of this failure, a theory has been widely entertained of late, which draws an analogy between the saturated molecules of two isomeric symmetrical disubstituted succinic acids and the unsaturated molecules of fumaric and maleic acids. According to this view, it is held that whilst, in general, a singly-bound atom or group can freely rotate, yet, under some circumstances, certain saturated molecules can be fixed in different phases. Thus, it is held that the disubstituted succinic acids

$$\begin{array}{c} \text{CHR}\cdot\text{COOH} \\ | \\ \text{CHR}\cdot\text{COOH} \end{array}$$
 may exist in two so-called stereochemical isomerides, of which the acid of lower-melting point usually gives an anhydride, and is therefore called the maleinöid or *cis* modification, whilst the acid of higher-melting point is incapable of forming an anhydride, and is named, on that account, the fumaröid or *trans*-modification. These two modifications may be represented thus.

Maleinöid or *cis*. Fumaröid or *trans*.

The isomerism in question, therefore, according to this view,
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depends on the fixation of carbon atoms united by single bonds, and the acceptance of this view involves the removal of one of the fundamental ideas of van't Hoff's theory.

A third theory—known as the theory of dynamical isomerism—has been advanced by Bischoff (*Ber.*, **23**, 624), but as the compounds which led him to adopt it have since been found not to exist (Auwers and Jackson, *Ber.*, **23**, 1606), it has not met with general acceptance.

It only remains to add, before proceeding to describe these derivatives in detail, that no attempt has yet been made to resolve any of the dialkyladipic acids into active forms.

EXPERIMENTAL.

As it appeared interesting to endeavour to obtain this acid for comparison with the other tetracarboxylic acids described in this paper, pure ethylic butanetetracarboxylate (1 mol.) was hydrolysed by boiling it for six hours with a solution of barium hydroxide (8 mols.), and the crystalline precipitate of the barium salt collected upon a filter, washed with water, and decomposed with sulphuric acid. After the slight excess of sulphuric acid had been carefully precipitated with barium hydroxide, the clear aqueous solution of the carboxylic acid was evaporated first on the water-bath, and then over sulphuric acid; in two days, it had crystallised in part in a mass of prismatic needles. These were separated from the mother-liquor, spread on a porous tile, and after drying further over sulphuric acid, were found to melt gradually between 140° and 160°.

0.1618 gave 0.2520 CO₂, and 0.0712 H₂O; C = 42.47; H = 4.88.

C₈H₁₀O₈ requires C = 41.03; H = 4.27 per cent.

C₇H₁₀O₆ ,, C = 44.21; H = 5.26 ,,

As the analysis appeared to indicate that a mixture of the tetracarboxylic and tricarboxylic acids had been formed, an attempt was made to isolate the tetracarboxylic acid from the mother liquor referred to above. The aqueous solution was evaporated further until a second crop of crystals had been deposited; the small quantity of mother liquor still remaining was poured off from this, and evaporated over sulphuric acid until it had completely solidified to a porcelain-like mass; this product was found to melt gradually, and evolved carbonic anhydride between 115° and 148°; at the latter temperature adipic acid melts, being formed from the carboxylic acids by elimination of carbonic anhydride

0.1567 gave 0.2471 CO_2 , and 0.0734 H_2O ; $\text{C} = 43.00$; $\text{H} = 5.20$ per cent.

A silver salt was prepared by pouring a neutral solution of the ammonium salt into a large excess of silver nitrate solution and shaking well; the white precipitate was collected on a filter, well washed, and dried first on a porous tile, and then over sulphuric acid.

0.3022 gave 0.1921 silver; $\text{Ag} = 63.06$.

0.1074 „ 0.0953 CO_2 and 0.0211 H_2O ; $\text{C} = 15.15$; $\text{H} = 1.36$.

$\text{C}_8\text{H}_6\text{O}_8\text{Ag}_4$ requires $\text{Ag} = 65.23$; $\text{C} = 14.50$; $\text{H} = 0.91$.

$\text{C}_7\text{H}_7\text{O}_8\text{Ag}_3$ „ $\text{Ag} = 63.40$; $\text{C} = 16.44$; $\text{H} = 1.36$.

It appears, therefore, that the butanetetracarboxylic acid, obtained by the hydrolysis of its ethylic salt with excess of barium hydroxide, is somewhat unstable, and tends to part with one molecule of carbonic anhydride, with formation of butanetricarboxylic acid. This instability of butanetetracarboxylic acid is in accordance with the character of its homologues. Conrad and Bischoff (*Annalen*, **214**, 71) have shown that ethanetetracarboxylic acid on hydrolysis with potassium hydroxide gives ethanetricarboxylic acid; Buchner (*Ber.*, **25**, 1157), however, found that the stability of the acid depends much on the concentration of the alkali, and if dilute sodium hydroxide be used, ethanetetracarboxylic acid may be isolated. Propanetetracarboxylic acid has been obtained by Kleber (*Annalen*, **246**, 107), who found that on slightly warming the aqueous solution of the acid, it is decomposed with evolution of carbonic anhydride. The hydrolysis of ethylic butanetetracarboxylate with alcoholic potash has been carried out by Perkin (*Trans.*, 1887, **51**, 19), and there was evidence of a partial conversion of the tetracarboxylic acid into the tricarboxylic acid; Perkin and Prentice (*Trans.*, 1891, **59**, 824), when hydrolysing ethylic pentanetetracarboxylate with alcoholic potash, obtained a similar result.

This mixture of butanetetracarboxylic acid and butanetricarboxylic acid is extremely soluble in water, giving a solution of intensely acid character. It is also very readily soluble in ether, and in methylic or ethylic alcohol, but insoluble in benzene, toluene, or light petroleum.

A neutral solution of the ammonium salts gives but a slight precipitate in the cold with barium chloride: on boiling, however, a copious white crystalline precipitate of the monobarium salts is thrown down. Calcium chloride gives no precipitate in the cold, but the calcium salts are precipitated on boiling, and dissolve again partially on cooling. Ferric chloride and copper acetate give no precipitate.

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The quantities used in the preparation of this substance were—

Ethylic butanetetracarboxylate	35.0 grams
Sodium dissolved in 60 c.c. alcohol....	4.6 „
Methylic iodide	28.4 „

The ethylic butanetetracarboxylate was dissolved in the sodium ethoxide, and the methylic iodide added slowly, since much heat is developed; it was then heated on the water-bath, using a reflux condenser, for about two hours, until it no longer gave an alkaline reaction. Water was then added, the product evaporated, extracted with ether, and the ethereal solution dried with calcium chloride. On distilling off the ether, and allowing the residual oil to stand some days, ethylic dimethylbutanetetracarboxylate crystallised out in beautiful prisms. It was collected on a filter, and washed with a little ether. For analysis, a portion was dried at 100°, and allowed to solidify.

0.1553 gave 0.3290 CO₂ and 0.1184 H₂O. C = 57.75; H = 8.04.
C₁₈H₃₀O₈ requires C = 57.75; H = 8.02 per cent.

The mother liquors from this substance, on standing, deposited a less pure product, which was used in the subsequent preparation of the dimethyladipic acids.

Ethylic dimethylbutanetetracarboxylate crystallises in beautiful, thick, four-sided prisms, melts at 54°, and is readily soluble in ether, methylic and ethylic alcohols, benzene, and toluene. It dissolves readily in warm light petroleum, and crystallises out again on cooling.

Ethylic dimethylbutanetetracarboxylate is not readily hydrolysed by barium hydroxide; in order to prepare the acid, the pure ethereal salt (1 mol.) was digested for three hours with an excess of a solution of pure potassium hydroxide (6 mols.) in methylic alcohol, in a flask connected with a reflux condenser. The product was evaporated nearly to dryness, mixed with water, the solution again evaporated to a small bulk to remove the last traces of alcohol, acidified with hydrochloric acid, and extracted four times with pure ether. On distilling off the ether, the dimethylbutanetetracarboxylic acid was left as a yellowish crystalline mass; this was purified by dissolving it in a little water, and allowing the solution to evaporate slowly over sulphuric acid in a vacuum, when the pure acid gradually crystallised

out as a mass of minute white needles. These were collected, dried on a porous tile, and over sulphuric acid in a vacuum, and analysed with the following result.

0.1014 gave 0.1698 CO_2 and 0.0528 H_2O ; $\text{C} = 45.67$; $\text{H} = 5.78$.

$\text{C}_{10}\text{H}_{14}\text{O}_8$ requires $\text{C} = 45.80$; $\text{H} = 5.35$ per cent.

Dimethylbutanetetra-carboxylic acid is deposited as a felted mass of minute needles on slowly evaporating its concentrated aqueous solution. It decomposes at 200° with evolution of carbonic anhydride, is readily soluble in ether and in methylic or ethylic alcohol, but insoluble in benzene, toluene, and light petroleum.

The *basicity* of the acid was determined by titration with decinormal solutions of potassium hydroxide and hydrochloric acid.

0.1763 gram of substance required 0.1480 gram of KOH for neutralisation, phenolphthaleïn being used as the indicator: the final colour change was sharp. A quadribasic acid of the formula $\text{C}_6\text{H}_{10}(\text{COOH})_4$ requires 0.1507 gram of KOH to form a salt of the formula $\text{C}_6\text{H}_{10}(\text{COOK})_4$. On adding one or two drops of litmus solution to the solution of the quadribasic salt, which was neutral as indicated by phenolphthaleïn, there was a very distinct blue coloration, which only gradually became red on running in hydrochloric acid. It appears, therefore, that dimethylbutanetetra-carboxylic acid forms quadribasic salts, which are neutral to phenolphthaleïn, but alkaline to litmus.

Silver Salt, $\text{C}_{10}\text{H}_{10}\text{O}_8\text{Ag}_4$.—The acid was dissolved in dilute ammonia, and the solution placed over sulphuric acid in a vacuum. As soon as it was only slightly alkaline to litmus it was poured into a large excess of silver nitrate solution in a flask, and the mixture well shaken. The white precipitate was collected on a filter, well washed with water, and dried on a porous tile and over sulphuric acid in a vacuum.

Analysis proved the salt to be quadribasic.

0.1048 gave 0.0650 Ag ; $\text{Ag} = 62.02$.

$\text{C}_{10}\text{H}_{10}\text{O}_8\text{Ag}_4$ requires $\text{Ag} = 62.60$ per cent.

If a solution of calcium chloride is added to a cold neutral solution of the ammonium salt no precipitate is formed, but on heating a crystalline precipitate of the *calcium salt* is thrown down.

When heated with sulphuric acid, ethylic dimethylbutanetetra-carboxylate is readily hydrolysed, but at the same time it loses 2 mols. of carbonic anhydride and yields a mixture of dimethyladipic acids. The ethereal salt was therefore heated on a sand-bath in a reflux

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apparatus with equal parts of sulphuric acid and water for about three hours. On allowing the mixture to cool, a considerable quantity of dimethyladipic acid crystallised out.

Isolation of the modification of higher-melting point.—The acid which had crystallised on cooling was washed with a little water, dissolved in a solution of sodium carbonate, boiled with animal charcoal, and filtered; the filtrate was then acidified with hydrochloric acid, and the dimethyladipic acid which separated, collected on a filter, washed with a little water, and recrystallised from water. This acid melted at 130—135°, and as it was found to be only sparingly soluble in boiling benzene, it was digested two or three times with small quantities of boiling benzene, and the benzene solution in each case poured off as completely as possible. The acid which still remained undissolved was recrystallised from water, and dried at 100°. It was then found to melt sharply at 142°.

Analysis showed it to consist of pure dimethyladipic acid.

0.1504 gave 0.1129 H₂O and 0.3053 CO₂; C = 55.36; H = 8.34.

C₈H₁₄O₄ requires C = 55.18; H = 8.04 per cent.

This acid has already been prepared by Zelinsky (*Ber.*, **24**, 3997), by the hydrolysis of ethylic dicyanodimethyladipate.

Isolation of the modification of lower-melting point.—The hot benzene solutions obtained in the isolation of the modification of dimethyladipic acid of higher-melting point, on cooling, deposited crystals which consisted chiefly of this modification. When these were removed, and the benzene evaporated on the water-bath, a yellowish, viscid oil was obtained, which crystallised completely on cooling, and melted at 80—90°. It was digested with a small quantity of cold benzene, the solution filtered from undissolved matter, and the benzene evaporated; the crystalline residue, on being again submitted twice to the same treatment, left a nearly colourless crystalline mass which melted at 70—72°, and was found by analysis to consist of pure dimethyladipic acid.

0.1383 gave 0.2805 CO₂ and 0.1028 H₂O; C = 55.31; H = 8.26.

C₈H₁₄O₄ requires C = 55.18; H = 8.04 per cent.

Zelinsky (*loc. cit.*), who separated the two isomeric dimethyladipic acids by recrystallisation from water, gives the melting-point of this dimethyladipic acid as 74—76°.*

* Since the printing of the thesis, Zitzing (*Ber.*, **27**, 1578; 1894) has described the preparation of ethylic dimethylbutanetetracarboxylate by the action of ethylenic dibromide on the monosodium derivative of ethylic methylmalonate, and he has prepared from it dimethylbutanetetracarboxylic acid and two dimethyladipic acids.

B. *Ethylic Diethylbutanetetra-carboxylate*, $\begin{array}{c} \text{CH}_2 \cdot \text{CEt}(\text{COOEt})_2 \\ | \\ \text{CH}_2 \cdot \text{CEt}(\text{COOEt})_2 \end{array}$.

The following quantities were employed in the preparation of this substance:

Ethylic butanetetra-carboxylate.....	70.0 grams
Sodium dissolved in 120 c.c. alcohol .	9.2 „
Ethylic iodide.....	70.0 „

The ethylic butanetetra-carboxylate was dissolved in the sodium ethoxide, and the ethylic iodide added cautiously with constant cooling, as much heat is evolved; the mixture was then heated for two hours on the water-bath, using a reflux condenser, and to ensure the completion of the action a little more ethylic iodide was added, and the digestion continued for two hours longer.

The product, mixed with water and evaporated to remove alcohol, gave a beautifully crystalline cake on cooling; this was separated from the mother liquor, dissolved in ether, and the ethereal solution, after being well washed with water, was dried with calcium chloride. On slowly evaporating the ethereal solution, the ethylic diethylbutanetetra-carboxylate separated in fine silky needles.

For analysis, the ethereal salt was recrystallised from ether, heated in a steam-oven to fusion, and allowed to solidify.

0.1307 gave 0.2865 CO_2 and 0.1030 H_2O ; $\text{C} = 59.78$; $\text{H} = 8.76$.

$\text{C}_{20}\text{H}_{34}\text{O}_8$ requires $\text{C} = 59.70$; $\text{H} = 8.45$ per cent.

Ethylic diethylbutanetetra-carboxylate crystallises from ether in fine silky needles, which melt at about $93-94^\circ$. It is readily soluble in hot methylic or ethylic alcohol, and crystallises out, on cooling, in fine needles. It is also readily soluble in cold benzene and toluene, and crystallises well from hot light petroleum.

Diethylbutanetetra-carboxylic acid, $\begin{array}{c} \text{CH}_2 \cdot \text{CEt}(\text{COOH})_2 \\ | \\ \text{CH}_2 \cdot \text{CEt}(\text{COOH})_2 \end{array}$.

Diethylbutanetetra-carboxylic acid was obtained by the hydrolysis of its ethereal salt with barium hydroxide. As this takes place with some difficulty, the ethylic salt was heated with twice the theoretical amount of barium hydroxide, for two days on the sand-bath, using a reflux condenser; during the action, a strong menthol-like odour was observed. When the hydrolysis was complete, the heavy crystalline precipitate of barium diethylbutanetetra-carboxylate was collected, and, after being washed with a little water, was ground up, suspended in water, and boiled for two hours with a slight excess of sulphuric acid so as to set free the diethylbutanetetra-carboxylic acid. The

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excess of sulphuric acid was exactly precipitated with barium hydroxide, and the aqueous solution evaporated to a small bulk on the water-bath; as the concentration proceeded, the acid crystallised in beautiful slender needles; these were collected on a filter, washed with a little water, and spread on a porous plate. On determining their melting-point, the acid frothed up in the capillary tube, and decomposed at 207—209°. After recrystallisation from water, the decomposing-point was unchanged. For analysis, the crystals were dried at 100°.

0.1442 gave 0.2619 CO₂ and 0.0850 H₂O; C = 49.53; H = 6.54.

C₁₂H₁₈O₈ requires C = 49.66; H = 6.20.

It is remarkable that diethylbutanetetracarboxylic acid is only sparingly soluble in water, whereas the corresponding dimethylbutanetetracarboxylic acid is so very readily soluble. It crystallises from its hot aqueous solution in needles, which decompose at 207—209°, with evolution of carbonic anhydride; it is soluble in ether, benzene, toluene, and light petroleum, and readily in methylic or ethylic alcohol.

The *basicity* of the acid was determined by titration with decimal solutions of potassium hydroxide and hydrochloric acid.

0.2139 gram of acid required 0.0850 gram of KOH for neutralisation, using litmus; litmus proved, however, a very unsatisfactory indicator, as, after dissolving the acid in excess of alkali, on titrating back with hydrochloric acid, the blue tint changed only gradually to red. An acid of the formula C₈H₁₄(COOH)₄ would require 0.0826 gram of KOH to form the bibasic salt, C₈H₁₄(COOH)₂(COOK)₂.

A determination was also made in which phenolphthalein was used as the indicator.

0.2114 gram of acid required 0.1656 gram of KOH for neutralisation. An acid of the formula C₈H₁₄(COOH)₄ would require 0.1632 gram of KOH to form the quadribasic salt, C₈H₁₄(COOK)₄. The solution of the acid in potassium hydroxide, after it had been neutralised with hydrochloric acid as shown by phenolphthalein, was coloured distinctly blue on the addition of one or two drops of litmus solution.

It appears, therefore, that diethylbutanetetracarboxylic acid, like dimethylbutanetetracarboxylic acid, forms quadribasic salts, which are neutral to phenolphthalein, but alkaline to litmus, the bibasic salt being neutral to litmus.

Silver salt, C₁₂H₁₄O₈Ag₄.—This was prepared exactly in the manner described on p. 1005, but it was found impossible to analyse it by ignition in a combustion furnace or in a crucible, as it decomposes with a rapidity which is almost explosive. The silver was therefore estimated as silver chloride. Analysis proved the salt to be quadribasic.

0.1180 gave 0.0935 AgCl; Ag = 59.57.

$C_{12}H_{16}O_8Ag_2$ requires Ag = 42.86 per cent.

$C_{12}H_{14}O_8Ag_4$ „ Ag = 60.17 per cent.

The silver salt decomposes slowly on exposure to light.

Calcium salt, $C_{12}H_{14}O_8Ca_2 + 5H_2O$ (?).—If calcium chloride is added to a cold neutral solution of ammonium diethylbutanetetra-carboxylate there is no precipitate, but, on boiling, a white micro-crystalline precipitate of the calcium salt is at once thrown down; this was collected on a filter, and dried on a porous plate. For analysis, the salt was dried by exposure to the air for four days.

As the quantity available for analysis was very small, it was impossible to determine the water of crystallisation accurately. An estimation of the calcium proved the salt to be tetrabasic, and indicated that it probably contains 5 mols. of water of crystallisation. Heated at 150° , the calcium salt lost more than 15 per cent. in weight, through the elimination of a portion of its water of crystallisation. It did not decompose when heated to 160° .

0.1083 gave 0.0630 $CaSO_4$; Ca = 17.11.

$C_{12}H_{16}O_8Ca$ requires Ca = 12.19.

$C_{12}H_{14}O_8Ca_2 + 5 H_2O$ requires Ca = 17.54; H_2O = 19.53 per cent.

In order to prepare these acids, the pure diethylbutanetetra-carboxylic acid was heated in an oil-bath at 210° until the evolution of carbonic anhydride had completely ceased. On cooling, the product solidified to a brownish crystalline cake.

Isolation of the modification of higher-melting point.—This brownish product was digested with boiling water, filtered while hot, and allowed to cool, when a considerable quantity of diethyladipic acid crystallised out in fine white needles; this, when separated from the mother-liquor, and dried on a porous plate, was found to melt at 122 — 129° ; after three more crystallisations the crystals melted sharply at 136° , and the melting-point was not altered by further crystallisation. An analysis proved it to be pure diethyladipic acid.

0.1503 gave 0.3257 CO_2 and 0.1178 H_2O ; C = 59.10; H = 8.70.

$C_{10}H_{18}O_4$ requires C = 59.40; H = 8.92 per cent.

Isolation of the modification of lower-melting point.—This proved to be a matter of greater difficulty. The aqueous mother-liquors, obtained in the isolation of the acid melting at 136° , were extracted three times with ether, and the ethereal solution evaporated; the yellowish oily residue after a time deposited a few stellate groups of

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crystals, and at the end of two days the oil had completely solidified. A small portion, after drying on a porous plate, was found to melt at $55-105^{\circ}$. The solubilities of this crude product, and of the pure acid melting at 136° , in various solvents, were then carefully compared, and it was found that the former was readily soluble in cold benzene, whilst the acid melting at 136° was only sparingly soluble in boiling benzene. Accordingly, the crude acid melting at $55-105^{\circ}$ was ground up and digested with cold benzene, and the solution filtered from a small quantity of undissolved acid, which, after drying, melted at $130-132^{\circ}$. The benzene solution evaporated on the water-bath, yielded a yellowish viscid mass, which crystallised when exposed over sulphuric acid in a vacuum; it melted at $45-60^{\circ}$ after it had been left on a porous plate for a time. The product was again digested with cold benzene, and the solution worked up in the same manner; on repeating the process, using little more than its own volume of benzene, a crystalline mass was finally obtained which melted at $45-46^{\circ}$. As the acid had still a yellowish tint, an attempt was made to purify it by means of the calcium salt. The acid was therefore digested with a large volume of lime water, and after carbonic anhydride had been passed through the solution, the filtrate was concentrated until the greater portion of the calcium salt had crystallised, and only about 2 c.c. of yellowish mother-liquor were left. The crystalline salt was collected on a filter, and washed with a little cold water. To obtain the pure diethyladipic acid, the calcium salt was dissolved in water, decomposed with hydrochloric acid, and extracted with ether; the ethereal solution when dried over anhydrous calcium chloride, evaporated, and exposed in a vacuum over sulphuric acid, left a colourless oil which gradually solidified to a mass of characteristic stellate groups of acicular crystals melting at $51-53^{\circ}$. For analysis, the acid was heated to fusion in a steam-oven, and allowed to solidify.

0.1218 gave 0.2631 CO_2 and 0.0987 H_2O ; $\text{C} = 58.91$; $\text{H} = 9.00$.

$\text{C}_{10}\text{H}_{18}\text{O}_4$ requires $\text{C} = 59.40$; $\text{H} = 8.92$ per cent.

Properties of the Diethyladipic acid melting at 136° .—This acid crystallises in six-sided prisms of the following form.

The *silver salt*, $C_{10}H_{16}O_4Ag_2$, was formed by dissolving the acid in slight excess of ammonia, and, after removing this excess by evaporation over sulphuric acid, adding excess of silver nitrate solution, when the silver salt was thrown down as a voluminous white precipitate. This was collected on a filter, washed with water, and dried first on a porous plate, and then over sulphuric acid in a vacuum.

0.1644 gave 0.0848 Ag; $Ag = 51.58$.

$C_{10}H_{16}O_4Ag_2$ requires $Ag = 51.92$ per cent.

The *calcium salt*, $C_{10}H_{16}O_4Ca + 2H_2O$, was also prepared by dissolving the acid in a large quantity of water, adding excess of calcium hydroxide, and boiling the solution; the excess of calcium hydroxide was removed by passing carbonic anhydride through the solution, which was again boiled, filtered, and evaporated on the water-bath; as the concentration proceeded, calcium diethyladipate crystallised out in beautiful white prisms. It was dried by exposure to the air for five days.

0.3155, on drying at 150° , lost 0.0398 H_2O ; the anhydrous salt so obtained gave 0.1613 $CaSO_4$; $H_2O = 12.61$; $Ca = 15.03$.

$C_{10}H_{16}O_4Ca + 2H_2O$ requires $H_2O = 13.04$; $Ca = 14.49$ per cent.

Unfortunately too little of the salt was left to allow of a second analysis. The calcium salt is very sparingly soluble in water.

Properties of the Diethyladipic acid melting about $51-53^\circ$.—This acid crystallises after fusion in large sub-octahedral masses, composed of interlacing needles, of the following form.

The formation of the *calcium salt* has already been described. It is more soluble in water than the calcium salt of the isomeric acid, which melts at 136° .

The *silver salt*, $C_{10}H_{16}O_4Ag_2$, was formed by the double decomposition of the aqueous solution of the calcium salt with silver nitrate solution; the precipitate, after being well washed, was dried on a porous plate and in a vacuum over sulphuric acid.

0.2450 gave 0.2535 CO_2 , 0.0852 H_2O , and 0.1276 Ag; $C = 28.22$; $H = 3.86$; $Ag = 52.07$.

$C_{10}H_{16}O_4Ag_2$ requires $C = 28.84$; $H = 3.84$; $Ag = 51.92$ per cent.

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The solubility of the two modifications of adipic acid in various solvents may be conveniently recorded in tabular form.

Solvent.	Solubilities of the two diethyladipic acids.	
	Diethyladipic acid melting at 136°.	Diethyladipic acid melting at 51—53°.
Ether	Readily soluble in the cold.	Readily soluble in the cold.
Methylic alcohol...	Readily soluble in the cold.	Readily soluble in the cold.
Ethylic alcohol...	Readily soluble in the cold.	Readily soluble in the cold.
Benzene	Very sparingly soluble; soluble in a large quantity of boiling benzene, and precipitated in minute needles on cooling.	Readily soluble in the cold.
Toluene.....	Sparingly soluble in the cold; readily soluble in hot toluene, and partially precipitated in crystals on cooling.	Readily soluble in the cold.
Light petroleum...	Insoluble even on boiling.	Soluble with difficulty on boiling, and partially precipitated in very minute needles on cooling.
Water.....	Soluble in much cold water; crystallises from a little hot water on cooling.	Readily soluble in the cold.

Attempt to prepare Ethylic Monethylbutanetetra-carboxylate,

In this communication, the preparation of several disubstituted derivatives of ethylic butanetetra-carboxylate is described, and it appeared of interest to ascertain whether monosubstituted derivatives would be obtained if the monosodium derivative of this substance were employed.

The following quantities were taken—

Ethylic butanetetra-carboxylate	35.0 grams.
Sodium dissolved in 30 c.c. alcohol...	2.3 „
Ethylic iodide.....	15.6 „

The ethylic butanetetra-carboxylate was dissolved in the sodium ethoxide, and the ethylic iodide added gradually; at first there was little evolution of heat, but, on shaking, the mixture became quite hot. It was heated on the water-bath for $2\frac{1}{2}$ hours, using a reflux condenser, the product evaporated on the water-bath, water added, and the evaporation repeated. The residue was then extracted

three times with ether, the ethereal solution washed with water, dehydrated with calcium chloride, and the ether evaporated first on the water-bath, and finally by exposure in a vacuum. In this way, about 35 grams of a yellowish oil were obtained, which deposited about 10 grams of crystals; these were separated from the mother-liquor by filtration with the pump, and freed from oil by spreading upon a porous plate. The product melted at 92—93°, and after repeated crystallisation from methylic alcohol the melting point remained constant at 93—94°. On analysis, it proved to be ethylic diethylbutanetetracarboxylate, corresponding with it in melting-point, crystalline form, and every other respect.

0·1641 gave 0·3601 CO₂ and 0·1246 H₂O; C = 59·84; H = 8·43.

C₁₈H₃₀O₈ requires C = 57·75; H = 8·02.

C₂₀H₃₄O₈ ,, C = 59·70; H = 8·45 per cent.

It is evident, therefore, that the main product of the action was the diethyl-, and not the monethyl-derivative of ethylic butanetetracarboxylate.

To determine the nature of the 25 grams of yellowish oil from which the ethylic diethylbutanetetracarboxylate had crystallised, and which should consist, if the above conclusion is correct, of unchanged ethylic butanetetracarboxylate, together with a certain amount of its diethyl derivative in solution, the oil was hydrolysed with barium hydroxide.

The 25 grams of oil were boiled with a concentrated solution of 75 grams of barium hydroxide for two days; a slight excess of sulphuric acid was then added to liberate the organic acids, and the filtered solution extracted 20 times with ether. The last 15 extracts were worked up together, and, after evaporating the ether, gave a nearly-colourless oil, which crystallised on standing. This product was heated at 210° in an oil-bath until the evolution of carbonic anhydride had ceased, and the residual dark-coloured oil, which solidified on cooling, after being spread on a porous plate, was dissolved in a little hot water, and allowed to evaporate slowly over sulphuric acid; the colourless crystalline deposit which formed was collected, and dried over sulphuric acid. It melted at 148°, and consisted of pure adipic acid, as is shown by the following analysis.

0·1441 gave 0·2613 CO₂ and 0·0901 H₂O; C = 49·45; H = 6·94.

C₆H₁₀O₄ requires C = 49·31; H = 6·86 per cent.

It appears, therefore, that, under the conditions employed, ethylic monethylbutanetetracarboxylate is not formed, the interaction, on the contrary, giving rise to ethylic diethylbutanetetracarboxylate, one half of the ethylic butanetetracarboxylate remaining unchanged.

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C. *Ethylic Dicetylbutanetetracarboxylate*, $\begin{matrix} \text{CH}_2\cdot\text{C}(\text{C}_{16}\text{H}_{33})(\text{COOEt})_2 \\ | \\ \text{CH}_2\cdot\text{C}(\text{C}_{16}\text{H}_{33})(\text{COOEt})_2 \end{matrix}$

The following quantities were used in the preparation of this substance,

Ethylic butanetetracarboxylate	35.0 grams.
Sodium dissolved in 120 c.c. alcohol ..	4.6 "
Cetylic iodide.....	76.0 "

The ethylic butanetetracarboxylate was dissolved in the cold solution of sodium ethoxide, the cetylic iodide added cautiously, and the mixture well shaken; no appreciable rise of temperature occurred; the mixture was then heated for six hours on the water-bath, using a reflux condenser. After cooling and standing over night, a considerable quantity of a crystalline powder had separated. The contents of the flask were mixed with water, gently heated on the water-bath to remove alcohol, and then extracted four times with ether. The ethereal extract was washed with water, dried with calcium chloride, and the ether distilled off, when about 60 grams of a dark oily liquid remained; this, after some days, deposited a considerable quantity of a yellowish, soap-like mass, which was separated from the oil by aid of the pump, spread upon a porous plate, and crystallised once or twice from light petroleum. The ethylic dicetylbutanetetracarboxylate was thus obtained pure in glistening white crystals.

For analysis, the crystals were heated to 100°.

0.1092 gave 0.2908 CO₂ and 0.1117 H₂O; C = 72.62; H = 11.36.

C₄₈H₉₀O₈ requires C = 72.54; H = 11.33 per cent.

Ethylic dicetylbutanetetracarboxylate crystallises from light petroleum in small, four-sided plates, which melt at 69.5°. It is readily soluble in ether, benzene, and toluene, and in hot light petroleum, glacial acetic acid, and methylic or ethylic alcohol; on cooling, it crystallises again from all these solvents.

Dicetylbutanetetracarboxylic acid, $\begin{matrix} \text{CH}_2\cdot\text{C}(\text{C}_{16}\text{H}_{33})(\text{COOH})_2 \\ | \\ \text{CH}_2\cdot\text{C}(\text{C}_{16}\text{H}_{33})(\text{COOH})_2 \end{matrix}$

To prepare this acid, pure ethylic dicetylbutanetetracarboxylate (1 mol.) was digested for about four hours with an excess of a solution of pure potassium hydroxide (6 mols.) in methylic alcohol, in a flask connected with a reflux condenser. After standing over night, a quantity of potassium dicetylbutanetetracarboxylate had crystallised out; this was collected, dissolved in hot water, and acidified with hydrochloric acid, when dicetylbutanetetracarboxylic acid separated as an oil, which, on cooling, solidified to a hard, white, non-

crystalline cake. To free the acid from traces of potassium chloride, the cake was kneaded with a little water, extracted with ether, and the ethereal solution washed with water. After removal of the ether by evaporation, and drying by exposure in a vacuum over sulphuric acid, pure dicetylbutanetetra-carboxylic acid was obtained as a beautiful, white, non-crystalline mass. It was found necessary to follow the above method, starting with pure material and utilising only the purest products, in order to prepare *pure* dicetylbutanetetra-carboxylic acid, as no solvent was found by means of which the crude acid could be purified by crystallisation.

On analysis—

0.0990 gave 0.2552 CO_2 and 0.1007 H_2O ; $\text{C} = 70.30$; $\text{H} = 11.17$.

$\text{C}_{40}\text{H}_{74}\text{O}_8$ requires $\text{C} = 70.38$; $\text{H} = 10.85$ per cent.

A further quantity of dicetylbutanetetra-carboxylic acid, sufficiently pure for subsequent operations, was obtained from the crude dark-coloured oily product, referred to as being obtained in the course of the preparation of pure ethylic dicetylbutanetetra-carboxylate. After hydrolysis of the oil with alcoholic potash, water was added, and the alcohol removed by evaporation on the water-bath. On cooling, almost the whole of the potassium dicetylbutanetetra-carboxylate separated as a yellow saponaceous mass, which was freed from cetylic iodide, cetylic alcohol, cetene, and other impurities, by repeatedly digesting it with ether until it became almost colourless. The free acid obtained from this potassium salt was an almost colourless mass.

Dicetylbutanetetra-carboxylic acid is a white soap-like body, which has not been obtained in a crystalline form. It does not possess a sharp melting-point, melting gradually between 80° and 90° , and when heated to 150° , decomposes with rapid evolution of carbonic anhydride. It is readily soluble in benzene, toluene, light petroleum, ether, and glacial acetic acid, insoluble in water, and concentrated hydrochloric and hydrobromic acids. It is readily soluble in cold ethylic alcohol, but in methylic alcohol its solubility varies extraordinarily within a very small range of temperature. Thus, whereas at 23° , 100 grams of methylic alcohol will dissolve 4.2 grams of the acid, at 19° only 1.9 grams of the acid are retained in solution.

The *basicity* of the acid was determined by titration with decinormal solutions of potassium hydroxide and hydrochloric acid.

0.2141 gram of substance required 0.0701 gram of KOH for neutralisation, phenolphthalein being used as the indicator. A quadribasic acid of the formula $\text{C}_{40}\text{H}_{74}\text{O}_8$ would take 0.0703 gram of KOH to form the quadribasic salt $\text{C}_{36}\text{H}_{70}(\text{COOK})_4$. On adding 1 or 2 drops of litmus solution to the solution of the quadribasic

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salt, which was neutral as indicated by phenolphthaleïn, a very distinct blue coloration appeared, which only gradually became red as hydrochloric acid was run in.

It appears, therefore, that dicetylbutanetetracarboxylic acid, like diethyl- and dimethyl-butane-tetracarboxylic acids, forms quadribasic salts, which are neutral to phenolphthaleïn, but alkaline to litmus.

Salts of Dicetylbutanetetracarboxylic acid.—In connection with the results obtained when determining the basicity of the acid, it appeared of interest to examine some of its salts.

Calcium salt, $C_{40}H_{72}O_8Ca$.—The acid was dissolved in dilute ammonia, and the excess of ammonia removed by evaporation, until the solution was but very slightly alkaline to litmus; excess of calcium chloride was then added, and the mixture well shaken. The white precipitate, collected on a filter, washed with water, and dried on a porous plate, was freed from a trace of colouring matter by crystallising it from boiling ethylic alcohol, from which it separated in needles.

For analysis, the salt was dried in the air for six days.

(1.) 0.3176 gave 0.0462 $CaSO_4$; $Ca = 4.31$.

(2.) 0.2887 „ 0.0424 „ „ 4.32.

(3.) When heated at 100° , the calcium salt slowly loses weight, becoming slightly viscid, and undergoes slow decomposition, so that it may possibly contain water or alcohol of crystallisation.

$C_{40}H_{72}O_8Ca$ requires $Ca = 4.83$ per cent.

It thus appears that the calcium salt which is formed under the above conditions is bibasic. It is insoluble in water, somewhat readily soluble in ether, but only sparingly in ethylic alcohol.

Silver salt, $C_{40}H_{72}O_8Ag_2$.—The solution of the ammonium salt, which was neutral as indicated by litmus, was poured into excess of silver nitrate solution, and the mixture well shaken. The insoluble silver salt which was thrown down was collected on a filter, well washed, and dried on a porous plate and over sulphuric acid.

0.1068 gave 0.0260 silver; $Ag = 24.34$.

$C_{40}H_{72}O_8Ag_2$ requires $Ag = 24.11$ per cent.

The silver salt formed under the above conditions appears, therefore, to be bibasic. It is unstable, and quickly blackens on exposure to light.

Pure dicetylbutanetetracarboxylic acid was heated in an oil-bath at 205° until carbonic anhydride was no longer evolved; on cooling, a

rather brown, non-crystalline cake was formed. With the exception of ether and methylic and ethylic alcohols, it is sparingly soluble in the usual solvents; in methylic or ethylic alcohol it is readily soluble on warming, separating again in an amorphous form on cooling; consequently the purification and isolation of the two isomeric dicetyl adipic acids is a matter of some difficulty. It was found advantageous to purify the mixture of the isomeric acids by digestion with ethylic alcohol and animal charcoal; after filtration, an almost colourless product separated on cooling, which melted gradually between 30° and 40° .

Isolation of the modification of higher melting-point.—The product melting at 30 — 40° was dissolved in hot ethylic alcohol, and the mass which separated on cooling, after drying on a porous plate and by exposure over sulphuric acid in a vacuum, was found to melt at 38 — 42° ; on repeating this treatment, a substance was obtained which melted at 41 — 43° , and subsequent recrystallisation did not raise the melting-point.

I. 0.1208 gave 0.3420 CO_2 and 0.1355 H_2O ; C = 77.21; H = 12.46.
 II. 0.1227 „ 0.3490 „ 0.1380 H_2O ; C = 77.54; H = 12.49.
 $\text{C}_{42}\text{H}_{52}\text{O}_4$ requires C = 77.53; H = 12.62 per cent.

From the results of the analysis, it appeared that the substance melting at 41 — 43° was not a dicetyl adipic acid, but its ethylic salt, formed by the repeated solution of the acid in hot ethylic alcohol, and this was rendered the more probable by its behaviour on hydrolysis. To obtain the acid itself, the ethereal salt was hydrolysed with alcoholic potash; the alcohol was evaporated on the water-bath, hydrochloric acid added, and the product extracted with ether; after washing the ethereal solution with water, the ether was evaporated on the water-bath, and the white mass obtained was dried by exposure over sulphuric acid in a vacuum; the melting-point, namely, 40 — 43° , was scarcely altered, but analysis proved it to be dicetyl adipic acid.

0.1138 gave 0.3203 CO_2 and 0.1267 H_2O ; C = 76.76; H = 12.37.
 $\text{C}_{38}\text{H}_{44}\text{O}_4$ requires C = 76.77; H = 12.46 per cent.

Isolation of the modification of lower melting-point.—In the isolation of the modification of higher melting-point, the substance melting at 30 — 40° , obtained by heating dicetylbutanetetracarboxylic acid at 210° , was dissolved in hot ethylic alcohol; the mass which separated on cooling melted at 38 — 42° , but the mother liquor, on standing a day or two, deposited a second crop, which was found to melt at 33 — 38° . The mother liquor from this was concentrated, and on standing deposited a third crop, melting at 29 — 34° ; this was

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dissolved in a small quantity of alcohol, and the solution, after a time, deposited a pure white amorphous substance, which, when dried, melted at 32—34°.

On analysis—

0.1491 gave 0.4188 CO₂ and 0.1675 H₂O; C = 76.65; H = 12.48.

C₃₈H₇₄O₄ requires C = 76.77; H = 12.46 per cent.

It is noteworthy that the lower-melting dicetyladipic acid, unlike the modification of higher melting-point, does not appear to form an ethereal salt when repeatedly dissolved in ethylic alcohol, though it is more readily soluble in the latter.

D. *Ethylic Dibenzylbutanetetracarboxylate*, $\begin{array}{c} \text{CH}_2\cdot\text{C}(\text{C}_7\text{H}_7)(\text{COOEt})_2 \\ | \\ \text{CH}_2\cdot\text{C}(\text{C}_7\text{H}_7)(\text{COOEt})_2 \end{array}$

The quantities used in the preparation of this substance were,

Ethylic butanetetracarboxylate	35.0 grams.
Sodium dissolved in 60 c.c. alcohol ...	4.6 „
Benzyl chloride	30.0 „

The ethylic butanetetracarboxylate was dissolved in the cold solution of the sodium ethoxide; the benzyl chloride was then cautiously added, and the mixture after shaking became perceptibly warm. The whole was then heated on the water-bath for about two hours, using a reflux condenser to complete the action. The contents of the flask were mixed with water, and distilled with steam until the alcohol and excess of benzyl chloride were removed; on cooling, the crystals which gradually separated were collected, washed with a little water, and dried on a porous plate. They were then dissolved in ether, the ethereal solution washed with water, dehydrated with anhydrous potassium carbonate, and the ether evaporated until the dibenzyl-derivative began to separate. On standing, a plentiful crop of small white crystals of pure ethylic dibenzylbutanetetracarboxylate was obtained; on analysis,

0.1934 gave 0.4830 CO₂ and 0.1282 H₂O; C = 68.09; H = 7.34.

C₃₀H₃₈O₈ requires C = 68.44; H = 7.22 per cent.

Ethylic dibenzylbutanetetracarboxylate crystallises in small four-sided tabular crystals. It is readily soluble in boiling methylic or ethylic alcohol, from which it crystallises on cooling. It is somewhat more sparingly soluble in ether and in light petroleum, from both of which it crystallises on cooling. It dissolves in warm benzene, but does not separate out on cooling. When crystallised from ethylic alcohol, it melts at 126—127°.

Dibenzylbutanetetracarboxylic acid, $\begin{matrix} \text{CH}_2\cdot\text{C}(\text{C}_6\text{H}_5)(\text{COOH})_2 \\ | \\ \text{CH}_2\cdot\text{C}(\text{C}_6\text{H}_5)(\text{COOH})_2 \end{matrix}$.

This acid is formed by the hydrolysis of ethylic dibenzylbutanetetracarboxylate with alcoholic potash. About 36 grams of the pure ethereal salt (1 mol.) were heated for two hours on the water-bath with a solution of 24 grams of potassium hydroxide (6 mols.) in methylic alcohol, in a flask connected with a reflux condenser. After cooling, and standing over night, a considerable quantity of potassium dibenzylbutanetetracarboxylate separated in the crystalline form; the alcoholic solution was filtered off, and worked up independently. The crystalline potassium salt was dissolved in water, and concentrated hydrochloric acid added, when the dibenzylbutanetetracarboxylic acid separated in a semi-solid state, and after standing for a short time solidified to a hard white crystalline cake. This was separated from the mother-liquor, washed with water, dried on a porous plate, and purified by repeated crystallisation from 75 per cent. acetic acid, until the melting-point was constant. It was found necessary to crystallise the acid six or seven times.

For analysis, the acid was dried on a porous plate, heated at 100° in an air-bath, and finally placed over potassium hydroxide in a vacuum, to ensure the removal of traces of acetic acid, which were retained somewhat persistently.

I. 0.1491 gave 0.3477 CO₂ and 0.0763 H₂O; C = 63.59; H = 5.68.

II. 0.1483 „ 0.3450 „ 0.0754 H₂O; C = 63.44; H = 5.64.

III. 0.1591 „ 0.3727 „ 0.0773 H₂O; C = 63.88; H = 5.39.

C₂₂H₂₂O₈ requires C = 63.77; H = 5.31 per cent.

A further quantity of less pure acid was obtained from the alcoholic mother-liquors previously referred to above; these were mixed with water, and after evaporating on a water-bath until free from alcohol, concentrated hydrochloric acid was added, when the dibenzylbutanetetracarboxylic acid separated as a heavy oil; this, when extracted with ether, &c., in the usual way, left the acid as a thick brownish oil, which did not solidify, even after standing for days over sulphuric acid in a vacuum. This crude acid was, however, sufficiently pure for conversion into dibenzyladipic acids as described in the next section.

Dibenzylbutanetetracarboxylic acid crystallises from dilute acetic acid in beautiful white plates, which, on exposure over potassium hydroxide in a vacuum, slowly lose weight, apparently from loss of acetic acid of crystallisation; after heating for a few minutes at 100°, the acid melts at 166—167°, with evolution of carbonic anhydride.

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Heated at 100—105°, it is very slowly converted into dibenzyladipic acids. It is readily soluble in cold ether, and in methylic or ethylic alcohol, also in hot benzene or toluene, and more sparingly in light petroleum, from which it crystallises on cooling. It is soluble in hot acetic acid, and crystallises out partially on cooling, but much more completely on the addition of water, as it is very sparingly soluble in water.

The *basicity of the acid* was determined by titration with decinormal solutions of potassium hydroxide and hydrochloric acid.

0.1800 gram of the acid required 0.0486 gram of KOH for neutralisation, as indicated by litmus. An acid of the formula $C_{18}H_{18}(COOH)_4$, would take 0.0974 gram of KOH to form the quadribasic salt, or 0.0487 gram of KOH to form the bibasic salt.

A determination was also made in which phenolphthaleïn was used as the indicator. 0.2389 gram of the acid required 0.0678 gram of KOH for neutralisation, as indicated by phenolphthaleïn; on adding a drop or two of litmus to the colourless solution, it was coloured distinctly blue, and two or three drops of N/10 hydrochloric acid were necessary to render the solution neutral to litmus. An acid of the formula $C_{18}H_{18}(COOH)_4$ would require 0.0646 gram of KOH to form the bibasic salt $C_{18}H_{18}(COOH)_2(COOK)_2$.

Whilst, therefore, phenolphthaleïn and litmus did not give absolutely identical results, it appears that dibenzylbutanetetracarboxylic acid tends to form neutral bibasic salts.

Salts of Dibenzylbutanetetracarboxylic acid.—In view of the result obtained on titrating the acid, it was thought advisable to examine some of its salts, in order to determine whether these were bibasic or quadribasic.

Calcium Salt, $C_{22}H_{20}O_8Ca + 2H_2O$.—About 2 grams of the acid were boiled with excess of calcium hydroxide, and the excess of lime precipitated by passing a stream of carbonic anhydride through the solution; the product was boiled and filtered, and the filtrate evaporated to a small bulk. The calcium salt which crystallised out was collected in a filter, and dried on a porous plate.

For analysis, the salt was dried by exposure to the air for six days. 0.3689, on heating at 110° till constant, lost 0.0286 H_2O ; $H_2O = 7.75$. 0.2838 salt gave 0.0788 $CaSO_4$; $Ca = 8.17$.

$C_{22}H_{20}O_8Ca + 2H_2O$ requires $Ca = 8.23$; $H_2O = 7.37$ per cent.

The calcium salt, which is formed in the above manner, appears therefore to be bibasic, crystallising probably with $2H_2O$. It loses its water of crystallisation very slowly over sulphuric acid in a vacuum; when heated at 150°, it gradually decomposes.

Silver Salt, $C_{22}H_{20}O_8Ag_2$.—Excess of silver nitrate solution was

added to a neutral solution of the calcium salt. The white precipitate was collected on a filter, well washed with water, and dried on a porous plate and finally over sulphuric acid.

Analysis proved the salt to be bibasic.

0.4038 gave, on ignition, 0.1389 silver; $\text{Ag} = 34.40$.

$\text{C}_{22}\text{H}_{20}\text{O}_8\text{Ag}_2$ requires $\text{Ag} = 34.55$ per cent.

The same silver salt is obtained on precipitating a neutral solution of the ammonium salt with silver nitrate solution; it is somewhat soluble in water, and decomposes readily when exposed to the light.

The impure oily dibenzylbutanetetracarboxylic acid (p. 1019) was heated in an oil-bath at 200° till all evolution of carbonic anhydride had ceased; on cooling, the impure dibenzyladipic acid solidified to a crystalline cake. The purification of this crude product, and the separation of the isomeric acids, is a somewhat difficult matter, and is best effected by means of their barium salts. About $1\frac{1}{2}$ times the theoretical quantity of barium hydroxide was dissolved in a considerable quantity of water, and boiled with the crude dibenzyladipic acids for $2\frac{1}{2}$ hours. As the barium salts thus formed remain dissolved if the solution is sufficiently dilute, the hot liquid was filtered, and a current of carbonic anhydride passed through the solution to remove the excess of barium hydroxide. The solution was filtered, the precipitated barium carbonate washed repeatedly with water, and the colourless filtrates concentrated on the water-bath until about one-half of the barium salts present had crystallised out. The glistening white plates thus obtained were rapidly filtered from the mother-liquor (the barium salts are less soluble in hot water than in cold), dissolved in water, and concentrated hydrochloric acid added, when the dibenzyladipic acids were thrown down as a white, microcrystalline precipitate; this was collected on a filter, washed with a little water, and dried on a porous plate; the melting-point was found to be $190\text{--}210^\circ$. After recrystallising three times from glacial acetic acid, a crop was obtained which melted at $207\text{--}211^\circ$; the mother-liquors were concentrated to a small bulk, and the acid which crystallised out again removed; the filtrate was then heated to boiling, and diluted with hot water until a cloudiness began to appear; on cooling, crystals were formed, which melted at $153\text{--}165^\circ$. The solubilities of the two crops melting at $207\text{--}211^\circ$ and $153\text{--}165^\circ$ respectively were then compared in several solvents, and it was found that the one melting at $207\text{--}211^\circ$ was practically insoluble in boiling toluene, whilst that melting at $153\text{--}165^\circ$ dis-

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solved readily, and in large measure crystallised out again on cooling.

To isolate the modification of dibenzyladipic acid of higher melting-point, the crop melting at $207-211^{\circ}$ was digested with boiling toluene, and the undissolved acid collected on a filter, washed, and dried; on repeating this process several times, the final product melted constantly at $211-213^{\circ}$. Analysis proved it to consist of pure dibenzyladipic acid.

0.1440 gave 0.3893 CO_2 and 0.0892 H_2O ; $\text{C} = 73.73$; $\text{H} = 6.88$.

$\text{C}_{20}\text{H}_{22}\text{O}_4$ requires $\text{C} = 73.62$; $\text{H} = 6.75$ per cent.

To isolate the modification of lower melting-point, the product melting at $153-165^{\circ}$ was recrystallised twice from toluene and then once from dilute acetic acid, when the acid was obtained in beautiful, colourless prisms melting sharply at 152° . It gave the following numbers on analysis.

0.1494 gave 0.4028 CO_2 and 0.0913 H_2O ; $\text{C} = 73.53$; $\text{H} = 6.79$.

$\text{C}_{20}\text{H}_{22}\text{O}_4$ requires $\text{C} = 73.62$; $\text{H} = 6.75$ per cent.

The mother liquor from the barium salts of the two acids gave a much larger quantity of the modification of lower melting-point.

Properties of the dibenzyladipic acid melting at $211-213^{\circ}$.—This acid is deposited from its glacial acetic acid solution in clusters of diamond-shaped crystals of the following form.

The *silver salt*, $\text{C}_{20}\text{H}_{20}\text{O}_4\text{Ag}_2$, which is very stable, was prepared from the ammonium salt in the same way as the other silver salts (p. 1011). It gave the following numbers on analysis.

0.2056 gave 0.0821 silver; $\text{Ag} = 39.93$.

$\text{C}_{20}\text{H}_{20}\text{O}_4\text{Ag}_2$ requires $\text{Ag} = 40.00$ per cent.

Properties of the dibenzyladipic acid melting at 152° .—This acid crystallises from dilute acetic acid in six-sided prisms of the following form.

The *silver salt*, $C_{20}H_{20}O_4Ag_2$, was prepared in the same way as the other silver salts, and analysed with the following result.

0.2620 gave 0.1049 Ag on ignition. $Ag = 40.03$.

$C_{20}H_{20}O_4Ag_2$ requires $Ag = 40.00$.

It is somewhat soluble in hot water, and blackens rapidly on exposure to light.

The *solubility* of the two dibenzyladipic acids in various solvents may be conveniently recorded in tabular form.

Solvents.	Solubilities of the two dibenzyladipic acids.	
	Dibenzyladipic acid melting at $211-213^\circ$.	Dibenzyladipic acid melting at 152° .
Ether	Soluble in the cold.	Readily soluble in the cold.
Methylic alcohol ..	Soluble in the cold.	Readily soluble in the cold.
Ethylic alcohol	Soluble in the cold.	Readily soluble in the cold.
Benzene	Insoluble.	Soluble on heating; the acid is not precipitated on cooling.
Toluene	Only slightly soluble on boiling.	Readily soluble on warming; on cooling the acid crystallises out again.
Light petroleum ...	Insoluble.	Insoluble.
Water	Insoluble.	Insoluble.
Glacial acetic acid..	Very sparingly soluble in the cold; on boiling it dissolves readily, and on cooling crystallises out again.	Readily soluble in cold acetic acid; it is precipitated in a crystalline form on adding water.

It will be seen from the above table that the two dibenzyladipic acids differ markedly in their degree of solubility in benzene, toluene, and glacial acetic acid; the acid melting at 152° being much the more soluble of the two.

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