XXIX.—*The Oxidation Products of the Methyl Homologues of Anhydracetonebenzil.*

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THE oxidation of anhydracetonebenzil, $\begin{array}{c} \text{C}_6\text{H}_5 \cdot \text{C} \equiv \text{CH} \\ | \\ \text{C}_6\text{H}_5 \cdot \text{C}(\text{OH}) \cdot \text{CH}_2 \end{array} > \text{CO}$, was studied by Japp and Lander (Trans., 1897, 71, 132). By oxidising it with sodium hypobromite, they obtained desyleneacetic acid, $\begin{array}{c} \text{C}_6\text{H}_5 \cdot \text{C} : \text{CH} \cdot \text{CO}_2\text{H} \\ | \\ \text{C}_6\text{H}_5 \cdot \text{CO} \end{array}$; whilst chromium trioxide, in acetic acid solution, was found to convert it into $\alpha\beta$ -diphenyl- $\alpha\beta$ -dihydroxyglutaric acid, $\begin{array}{c} \text{C}_6\text{H}_5 \cdot \text{C}(\text{OH}) \cdot \text{CO}_2\text{H} \\ | \\ \text{C}_6\text{H}_5 \cdot \text{C}(\text{OH}) \cdot \text{CH}_2 \cdot \text{CO}_2\text{H} \end{array}$.

We have now studied the oxidation of α -methylanhydracetonebenzil, $\begin{array}{c} \text{C}_6\text{H}_5 \cdot \text{C} \equiv \text{C}(\text{CH}_3) \\ | \\ \text{C}_6\text{H}_5 \cdot \text{C}(\text{OH}) \cdot \text{CH}_2 \end{array} > \text{CO}$ (m. p. 118° and 133.5°); β -methylanhydracetonebenzil, $\begin{array}{c} \text{C}_6\text{H}_5 \cdot \text{C} \equiv \text{CH} \\ | \\ \text{C}_6\text{H}_5 \cdot \text{C}(\text{OH}) \cdot \text{CH}(\text{CH}_3) \end{array} > \text{CO}$ (m. p. 180°); $\alpha\beta$ -dimethylanhydracetonebenzil, $\begin{array}{c} \text{C}_6\text{H}_5 \cdot \text{C} \equiv \text{C}(\text{CH}_3) \\ | \\ \text{C}_6\text{H}_5 \cdot \text{C}(\text{OH}) \cdot \text{CH}(\text{CH}_3) \end{array} > \text{CO}$ (m. p. 150°); and $\beta\beta$ -dimethylanhydracetonebenzil, $\begin{array}{c} \text{C}_6\text{H}_5 \cdot \text{C} \equiv \text{CH} \\ | \\ \text{C}_6\text{H}_5 \cdot \text{C}(\text{OH}) \cdot \text{C}(\text{CH}_3)_2 \end{array} > \text{CO}$ (m. p. 181°). (Compare the preceding paper; also Japp and Meldrum, Trans., 1901, 79, 1028.) The remaining methyl homologue, $\alpha\beta\beta$ -trimethylanhydracetonebenzil, owing to the difficulty of obtaining it in quantity, was not included in the investigation.

Of the foregoing homologues, only α -methylanhydracetonebenzil is attacked by potassium hypobromite. It yields α -desylenepropionic acid (m. p. 174.5°):

together with *diphenylmaleic acid*; the latter, when liberated from its salt, is converted into its anhydride. From its formation from a closed-chain compound of the above formula, α -desylenepropionic acid must have the configuration, $\begin{array}{c} \text{CH}_3 \cdot \text{C} \cdot \text{CO}_2\text{H} \\ | \\ \text{C}_6\text{H}_5 \cdot \text{C} \cdot \text{CO} \cdot \text{C}_6\text{H}_5 \end{array}$. The reaction is analogous to that in which anhydracetonebenzil is oxidised by hypobromite to desyleneacetic acid, but in the latter case no formation of diphenylmaleic acid was observed. The formation of diphenylmaleic acid involves a shifting of the double bonds in α -methylanhydracetone-

benzil, so as to form the group $\text{C}_6\text{H}_5 \cdot \underset{\text{O}}{\underset{\text{O}}{\text{C}}} \cdot \text{C}_6\text{H}_5$, the change being accompanied by a migration of the hydroxyl group. This change in the position of the double bonds in the *cyclopentene* ring is of frequent occurrence in the reactions of anhydracetonebenzil and its derivatives: thus, in the formation of diphenyl*cyclopentenone*,

and its homologues. The formation of diphenylmaleic acid (along with diphenylfumaric acid) from a compound belonging to this group, has already been observed in the oxidation of anhydracetonebenzil-carboxylic acid with alkaline hypobromite (Japp and Lander, *Trans.*, 1897, 71, 142).

Boiling with hydriodic acid converts α -desylenepropionic acid into 1-methyl-2:3-diphenyl- Δ^1 -crotonolactone* (m. p. 88.5°):

This reaction exactly corresponds with the formation of the stable diphenylcrotonolactone melting at 151.5° (according to Thiele, the Δ^1 -crotonolactone) by the action of hydriodic acid on desyleneacetic acid, except that in the latter case a portion of the diphenylcrotonolactone is hydrolysed to desylacetic acid (Japp and Lander, *Trans.*, 1897, 71, 156).

By warming methyl-diphenylcrotonolactone with alcoholic potassium hydroxide it is converted into Knoevenagel's α -desylpropionic acid:

On the other hand, when α -desylpropionic acid is distilled under reduced pressure it parts with water and is reconverted into *methyl-diphenylcrotonolactone*.

In the oxidation of anhydracetonebenzil with chromium trioxide, studied by Japp and Lander (*Trans.*, 1897, 71, 133), the closed chain opens at the point between the carbonyl and the ethylene group, and the latter group is hydroxylated, whilst at the same time its end carbon atom and the carbonyl group are oxidised to carboxyl

* The reasons for adopting the Δ^1 -unsaturated constitution for this stable lactone of α -desylpropionic acid, instead of the apparently more obvious Δ^2 -unsaturated constitution, reserving the latter for the isomeric labile lactone (not yet prepared), are to be found in Thiele's paper: "Ueber isomere Diphenylcrotonlactone" (*Annalen*, 1899, 306, 194).

groups, a dibasic acid resulting— $\alpha\beta$ -diphenyl- $\alpha\beta$ -dihydroxyglutaric acid :

We find that the oxidation of β -methylanhydracetonebenzil with chromium trioxide proceeds on strictly analogous lines :

In the case of the other methyl homologues of anhydracetonebenzil which we have examined, oxidation with chromium trioxide opens the closed chain in the same place ; but the further course of the reaction is governed both by the position and by the number of the methyl groups. Thus :

1. The presence of a methyl group in the α -position (*i.e.*, in the CH-group) of anhydracetonebenzil prevents the formation of a dibasic acid, and a ketonic acid is formed instead.

2. The presence of a methyl group in the α -position, or of two methyl groups in the β -position (*i.e.*, in the CH_2 -group), leads to the elimination of water from the resulting acid, so that the group

The following oxidations with chromium trioxide illustrate these rules :

* The action of alkyl groups in promoting the elimination of water—as, for example, in the case of homologues of maleic acid—is too familiar to call for remark.

† There is, so far as we are aware, no convenient nomenclature for “bridge-oxygen”—oxygen uniting two carbon atoms which are already either directly or indirectly united. We would suggest the prefix “oxido” as supplying this want. Thus glycidic acid would be “ $\alpha\beta$ -oxidopropionic acid,” the bridge-oxygen being thus regarded as a bivalent substituent. This prefix has the analogy of “imido” to recommend it.

The two foregoing oxidations illustrate Rules 1 and 2.

In oxidising *αβ*-dimethylanhydracetonebenzil with chromium trioxide, another portion of the substance yields a neutral compound, in the formation of which the closed chain is not opened :

The oxidation of *ββ*-dimethylanhydracetonebenzil, on the other hand, illustrates Rule 2 :

Here the oxidation follows the same course as in the cases of anhydracetonebenzil and *β*-methylanhydracetonebenzil, except that, under the influence of the two methyl groups, the resulting compound parts with water, passing into the oxido-form.

In the present introduction we will describe only those reactions of the foregoing oxidation products which admit of a theoretical interpretation.

By boiling methylphenyldihydroxyglutaric acid with fuming hydriodic acid it is converted into *methylphenylcrotonolactone* (m. p. 88·5°):

and as there is no reduction involved, hydrochloric acid effects the same transformation, although only very imperfectly. The reaction corresponds with that in which diphenyldihydroxyglutaric acid is converted, under the influence of hydracids, into a mixture of diphenyl-

Δ^1 -crotonolactone (m. p. 151.5°) and desylacetic acid (Japp and Lander, Trans., 1897, 71, 127).*

When acetodiphenyloxidobutyric acid is boiled with fuming hydriodic acid, it yields a mixture of *diphenyl- Δ^1 -crotonolactone* (m. p. 151.5°) and *desylacetic acid*, the aceto-group being eliminated, possibly in the form of aldehyde:

Acetodiphenyloxidobutyric acid forms a *semicarbazone*. It also interacts with phenylhydrazine; but we were unable to purify the resulting compound, a failure which is to be regretted, as the reactions of the other oxido-acids—acetomethyldiphenyloxidobutyric acid and dimethyldiphenyloxidoglutaric acid—with phenylhydrazine are quite abnormal, the oxido-group taking part in the reaction. Thus acetomethyldiphenyloxidobutyric acid

interacts with phenylhydrazine according to the equation:

yielding a *neutral compound* melting at 212° . As the acid thus interacts with phenylhydrazine with elimination of only 1 mol. of water, forming a compound which is no longer an acid, it is clear that the carbonyl of the aceto-group does not take part in the reaction, as the joint action of the carbonyl and carboxyl groups on a mol. of phenylhydrazine would involve the elimination of 2 mols. of water, not to mention the fact that the carbonyl group is in the δ -position to the carboxyl group, a circumstance which would render such joint action impossible. The following scheme would furnish an explanation of the reaction:

* The diphenylcrotonolactone is there represented, according to the view at that time prevailing as the Δ^2 -unsaturated compound.

Compound, m. p. 212°.

According to this explanation the basic imino-group of the phenylhydrazine first interacts additively with the oxido-group of the acid, as in the action of piperidine on phenylglycidic acid (Erlenmeyer, jun., *Annalen*, 1892, 271, 157); and then this intermediate compound parts with water forming a pyrazolidone ring, as in the interaction of the β -halogen-propionic acids with phenylhydrazine (*Ber.*, 1891, 24, Ref., 234).^{*} That the elimination of water from the hypothetical intermediate compound does not occur between carboxyl and hydroxyl so as to form a lactone is shown by the fact that the resulting compound does not yield a salt with alcoholic potash.

The corresponding abnormal reaction of dimethyldiphenyloxidoglutaric acid will be described further on.

Acetomethyldiphenyloxidobutyric acid yields an oxime in which the carbonyl of the aceto-group is oximated, the reaction, unlike that with phenylhydrazine just described, being perfectly normal. The oxime contains the carboxyl group and dissolves in sodium carbonate.

When heated, acetomethyldiphenyloxidobutyric acid parts with carbon dioxide, yielding β -aceto- α -ethyl- $\alpha\beta$ -diphenyloxidoethane, $\text{C}_6\text{H}_5 \cdot \text{C} \begin{array}{l} \text{---} \text{CO} \cdot \text{CH}_3 \\ \text{---} \text{O} \end{array} \text{C}_2\text{H}_5$ (m. p. 98—99°). This yields a *semicarbazone*, $\text{C}_{19}\text{H}_{21}\text{O}_2\text{N}_3$ (m. p. 204°).

Potassium hypobromite oxidises acetomethyldiphenyloxidobutyric acid to α -methyl- $\alpha'\beta$ -diphenyl- $\alpha'\beta$ -dihydroxyglutaric acid:

The product is identical with the acid obtained by the oxidation of β -methylanhydrazetonebenzil with chromium trioxide. It is to be noted how, in the present case, the removal of a methyl group leads to the re-hydration of the oxido-group.

When acetomethyldiphenyloxidobutyric acid is boiled with fuming hydriodic acid it yields *methyldiphenyl- Δ^1 -crotonolactone* (m. p. 88·5°):

^{*} One of us is at present engaged, conjointly with Mr. W. Maitland, in studying the action of phenylhydrazine on sodium phenylglycidate, and the results obtained, which we hope to publish shortly, entirely confirm the above interpretation.

This change corresponds with that which acetodiphenyloxidobutyric acid undergoes under the same conditions (*v. supra*), except that in the present case, owing to the dehydrating action of the methyl group, only the unsaturated lactone, and none of the corresponding ketonic acid, is formed.

By the action of acetic anhydride, mixed with a few drops of concentrated sulphuric acid, on acetomethyldiphenyloxidobutyric acid in the cold, a *lactone* of the formula $\text{C}_{21}\text{H}_{20}\text{O}_5$ (m. p. 140°) is formed according to the equation :

The foregoing process might be regarded as an addition of $\text{CH}_3 \cdot \text{CO}_2$ and H to the oxido-group, the resulting compound then parting with water to form a lactone :

When this lactone is treated with alcoholic potassium hydroxide it yields *α-desylpropionic acid*. Possibly methyldiphenyl- Δ^1 -crotonolactone is formed as an intermediate product :

the lactone being then hydrolysed to *α-desylpropionic acid* as already described.

The neutral compound obtained along with acetomethyldiphenyloxidobutyric acid by the oxidation of *αβ*-dimethylanhydracetonebenzil, is, as already stated, to be regarded as a dimethyldiphenyltrihydroxy-

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cyclopentanone. That the pentacarbon ring is still intact in this compound is shown by the fact that, by boiling the substance with hydriodic acid, it yields, along with other products, *dimethyldiphenylcyclopentenone* (m. p. 122°):

a compound which can also be obtained by the reduction of $\alpha\beta$ -dimethylanhydracetonebenzil. The latter reaction will be described in a subsequent communication, where the reasons for assigning to the compound the foregoing constitution will also be given.

Dimethyldiphenyltrihydroxycyclopentanone forms a *semicarbazone*, $\text{C}_{20}\text{H}_{23}\text{O}_4\text{N}_3$. It also yields a number of other transformation products; but, as the constitution of most of these admits of more than one interpretation, we will confine ourselves to describing later on the experimental results.

Dimethyldiphenyloxidoglutaric acid, $\begin{array}{c} \text{C}_6\text{H}_5 \cdot \text{C} - \text{CO}_2\text{H} \\ | \\ \text{C}_6\text{H}_5 \cdot \text{C} - \text{C}(\text{CH}_3)_2 \cdot \text{CO}_2\text{H} \end{array}$, the

oxidation product of $\beta\beta$ -dimethylanhydracetonebenzil, interacts with phenylhydrazine according to the equation:

yielding a *neutral* compound melting at 182°. The reaction resembles that of acetomethyldiphenyloxidobutyric acid already described, and in both cases the oxido-group takes part in the reaction. The mechanism of the process may, in the present case, be represented as follows:

As in the former case, so here also the first stage of the process may be assumed to be an additive interaction between the phenylhydrazine and the oxido-group of the acid; but in the present reaction the resulting intermediate compound parts with *two* mols. of water, yield-

ing a substance which contains both the lactone ring and the pyrazolidone ring. Its lactonic character is shown by the fact that it yields a salt with potassium hydroxide, and that the resulting acid, when freshly precipitated, dissolves in alkaline carbonates, but, on drying, or on recrystallisation, is reconverted into the neutral compound melting at 182°.

When heated, dimethyldiphenyloxidoglutaric acid parts with water,

yielding the *anhydride*
$$\begin{array}{c} \text{C}_6\text{H}_5 \cdot \text{C} \text{---} \text{CO} \\ \diagup \quad \diagdown \\ \text{O} \\ \diagdown \quad \diagup \\ \text{C}_6\text{H}_5 \cdot \text{C} \text{---} \text{C}(\text{CH}_3)_2 \text{---} \text{CO} \end{array} \text{O} \quad (\text{m. p. } 158^\circ),$$
 which

may also be obtained by the action of acetic anhydride, with the addition of a few drops of concentrated sulphuric acid, on the acid in the cold. Treated with alkalis the anhydride regenerates the acid.

By boiling with dilute sulphuric acid, dimethyldiphenyloxidoglutaric acid is converted, partly into the foregoing anhydride, and partly, with elimination of carbon dioxide and water, into 1 : 1-dimethyl-2 : 3-diphenyl- Δ^2 -crotonolactone, a little α -desylisobutyric acid being formed at the same time :

In this case, only the Δ^2 -crotonolactone can be formed, as there is no hydrogen attached to the α -carbon atom of α -desylisobutyric acid.

The formation of α -desylisobutyric acid from dimethyldiphenyloxidoglutaric acid is analogous to that of phenylacetaldehyde from phenylglycidic acid :

The formation of desylacetic acid from acetodiphenyloxidobutyric acid, and of α -desylpropionic acid (or rather of its lactone—methyl-diphenyl- Δ^1 -crotonolactone) from acetomethyldiphenyloxidobutyric acid (*v. supra*), belong to the same category, except that in the two latter cases, the aceto-group is eliminated in place of carbon dioxide.

The constitution of α -desylisobutyric acid was proved by synthesising it from sodium deoxybenzoin and ethyl α -bromisobutyrate, hydrolysing, with caustic alkali, the ester thus obtained :

By the action of acetic anhydride, containing a little concentrated sulphuric acid, on *α*-desylisobutyric acid in the cold, the foregoing *dimethyldiphenylcrotonolactone* (m. p. 105—106°) is formed.

When dimethyldiphenyloxidoglutamic acid is boiled with hydriodic acid, it yields, as first product of the reaction, *α*-desylisobutyric acid, the reaction so far resembling that of dilute sulphuric acid just described; but a reduction compound is formed at the same time, and if the boiling is continued sufficiently long, the *α*-desylisobutyric acid is converted into this reduction compound, which is the dimorphous *lactone* (m. p. 106° and 110°) of *αα*-dimethyl-*βγ*-diphenyl-*γ*-hydroxybutyric acid

This saturated lactone can also be obtained by reducing *α*-desylisobutyric acid in boiling alcoholic solution with sodium. A salt of the above dimethyldiphenylhydroxybutyric acid

is formed; the latter acid, when liberated, yields the lactone.

When the saturated lactone is reduced at a higher temperature with hydriodic acid and red phosphorus, it is converted into *αα*-dimethyl-*βγ*-diphenylbutyric acid (m. p. 172°):

On the other hand, if the saturated lactone is dissolved in potassium hydroxide, and the resulting salt of dimethyldiphenyl-*γ*-hydroxybutyric acid is oxidised with potassium permanganate, *α*-desylisobutyric acid is obtained:

EXPERIMENTAL.

I. α -METHYLANHYDRACETONEBENZIL, A. *Oxidation of α -Methylanhydracetonebenzil with Potassium Hypobromite.*

Five grams of finely-powdered α -methylanhydracetonebenzil were suspended in an alkaline solution of potassium hypobromite (prepared by adding 15 grams of bromine to a solution of 30 grams of potassium hydroxide in 300 c.c. of water), and the mixture was stirred for 24 hours by means of a mechanical stirrer. The unchanged substance was removed by filtration, and the filtrate, after addition of sulphurous acid, was acidified with hydrochloric acid. The pale yellow precipitate was dissolved in ether, and the ethereal solution was extracted first with sodium carbonate solution, and afterwards with a solution of sodium hydroxide. The acid obtained on acidifying the sodium carbonate extract was crystallised from a mixture of benzene and light petroleum ("ligroin"). It formed groups of slender needles melting constantly at 174.5° , and on analysis gave figures agreeing with the formula of α -desylenepropionic acid,

$$\begin{array}{c} \text{C}_6\text{H}_5 \cdot \text{C} : \text{C}(\text{CH}_3) \cdot \text{CO}_2\text{H} \\ \text{C}_6\text{H}_5 \cdot \text{CO} \end{array}.$$

0.1560 gave 0.4387 CO_2 and 0.0769 H_2O . $\text{C} = 76.69$; $\text{H} = 5.47$.

$\text{C}_{17}\text{H}_{14}\text{O}_3$ requires $\text{C} = 76.69$; $\text{H} = 5.26$ per cent.

The acid did not dissolve readily in dilute ammonia, and an attempt to prepare the silver salt from the ammonium salt by precipitation did not yield a pure product.

The sodium hydroxide extract above referred to yielded, on acidifying, a yellow precipitate which, on recrystallisation from benzene, was obtained in thick yellow needles showing a green fluorescence and melting at 156° . These are the properties of *diphenylmaleic anhydride*,

$$\begin{array}{c} \text{C}_6\text{H}_5 \cdot \text{C} \cdot \text{CO} \\ \text{C}_6\text{H}_5 \cdot \text{C} \cdot \text{CO} \end{array} > \text{O},$$

and, on mixing the substance with a sample of the latter compound, the melting point was not depressed.

0.1519 gave 0.4280 CO_2 and 0.0595 H_2O . $\text{C} = 76.84$; $\text{H} = 4.35$.

$\text{C}_{16}\text{H}_{10}\text{O}_3$ requires $\text{C} = 76.80$; $\text{H} = 4.00$ per cent.

Oxidation of 5 grams of α -methylanhydracetonebenzil yielded 0.4 gram of α -desylenepropionic acid and 1.6 gram of diphenylmaleic anhydride, whilst two grams of the original substance were recovered unchanged.

Reduction of α -Desylenepropionic Acid; Formation of 1-Methyl-2:3-di-

boiled with fuming hydriodic acid (sp. gr. 1.96) for 5 minutes. The product was dissolved in ether and treated with solutions of sulphurous acid and sodium carbonate. The residue obtained on evaporation of the ether was crystallised from methyl alcohol. Tabular crystals were deposited melting at $70-71^\circ$; but after standing for some weeks they turned opaque and then melted at 88.5° . The latter is the melting point of *methylidiphenylcrotonolactone*—a substance obtained in various other reactions in the course of this work. The present specimen was further identified by the mixture melting-point method, a sample of the compound prepared from acetomethylidiphenyloxidobutyric acid (*v. infra*) being employed for comparison.

The lower melting point of $70-71^\circ$ was not observed except in the case of the foregoing preparation.

B. Oxidation of α -Methylanhydracetonebenzil with Chromium Trioxide.

To a solution of 10 grams of α -methylanhydracetonebenzil * in glacial acetic acid, a solution of 15 grams of chromium trioxide in the same menstruum was very gradually added, the mixture being cooled with water and stirred during the process. The whole was allowed to stand in the cold for 3 days, after which it was poured into excess of water. The dark green, viscid precipitate was separated and extracted with ether, and the ethereal solution was shaken with aqueous sodium carbonate. On acidifying the alkaline solution an organic acid was precipitated as a pale green oil which afterwards solidified. This was redissolved in ether, the solution was re-extracted with sodium carbonate, and the alkaline solution was *gently* warmed for some time; this caused the separation of chromium compounds, which were removed by filtration. On acidifying, the acid, now free from chromium, was precipitated. (If the alkaline solution is too strongly heated in the foregoing process the acid obtained is yellow.) It crystallises from dilute alcohol, or from a mixture of ether and light petroleum, in slender needles melting at $131-132^\circ$ with decomposition. On several occasions it was noticed that on allowing the needles to stand in contact with the dilute alcoholic mother liquor, they were transformed into tabular crystals with the same melting point; these could be converted into needles by recrystallisation from the mixture of ether and light petroleum.

* In the earlier experiments the modification of α -methylanhydracetonebenzil melting at 118° was employed; in the later, that melting at 133.5° . (See preceding paper.) Both yielded the same product. The same applies to the hypobromite oxidation just described.

Analyses, in which different preparations were employed, gave figures agreeing with the formula of γ -aceto- $\beta\gamma$ -diphenyl- $\beta\gamma$ -oxidobutyric

0.1893 gave 0.5033 CO_2 and 0.0938 H_2O . C = 72.51; H = 5.50.

0.1519 „ 0.4073 CO_2 „ 0.0752 H_2O . C = 73.13; H = 5.50.

0.1966 „ 0.5249 CO_2 „ 0.0968 H_2O . C = 72.81; H = 5.47.

$\text{C}_{18}\text{H}_{16}\text{O}_4$ requires C = 72.97; H = 5.40 per cent.

The silver salt was obtained as a white precipitate on adding silver nitrate to a solution of the ammonium salt:

0.4169 gave 0.1109 Ag. Ag = 26.60.

$\text{C}_{18}\text{H}_{15}\text{O}_4\text{Ag}$ requires Ag = 26.78 per cent.

The yield of pure acid from 10 grams of α -methylanhydracetonebenzil was only 0.5 gram. Owing to the difficulty of obtaining the acid in quantity we have been unable to study it with the requisite thoroughness, and the constitution which we assign to it is based chiefly on its analogy to its homologue acetomethyldiphenyloxidobutyric acid, the product of the oxidation of $\alpha\beta$ -dimethylanhydracetonebenzil with chromium trioxide.

oxidobutyric Acid.—0.7 gram of semicarbazide hydrochloride was dissolved in a very little warm water and mixed with an alcoholic solution of 0.6 gram of potassium acetate. After filtering off the potassium chloride, the filtrate was added to an alcoholic solution of 0.6 gram of the foregoing acid, and the mixture was allowed to stand. After two days the crystals which had formed were separated and recrystallised from alcohol, from which they were deposited in groups of small needles melting at 198° with decomposition. The compound was soluble in sodium carbonate, showing that the carboxyl group had not taken part in the reaction.

A nitrogen determination gave figures which were somewhat lower than those required by the semicarbazone; but we had no acid to spare for a second preparation.

0.1368 gave 13.6 c.c. moist nitrogen at 21° and 760 mm. N = 11.32.

$\text{C}_{19}\text{H}_{19}\text{O}_4\text{N}_3$ requires N = 11.89 per cent.

Action of Hydriodic Acid on Acetodiphenyloxidobutyric Acid: Formation of Desylacetic Acid,
$$\begin{array}{c} \text{C}_6\text{H}_5 \cdot \text{CO} \\ | \\ \text{C}_6\text{H}_5 \cdot \text{CH} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H} \end{array}$$
 and Diphenyl- Δ^1 -croto-

$$\begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{C}_6\text{H}_5 \cdot \text{CH} \quad \text{CO} \\ \diagdown \quad \diagup \\ \text{C}_6\text{H}_5 \cdot \text{C} = \text{CH} \end{array}$$
 lactone, —Acetodiphenyloxidobutyric acid was boiled with excess of fuming hydriodic acid for 2 minutes. The product was dissolved in ether and treated with sulphurous acid; sodium carbonate then removed an organic acid, whilst a neutral substance remained in the ether. The acid crystallised from alcohol in the lustrous octahedra of *desylacetic acid*, melting at 161° ; and its melting point was not altered by mixing it with a specimen of desylacetic acid.

0.1532 gave 0.4254 CO_2 and 0.0774 H_2O . $\text{C} = 75.72$; $\text{H} = 5.61$.

$\text{C}_{16}\text{H}_{14}\text{O}_3$ requires $\text{C} = 75.59$; $\text{H} = 5.51$ per cent.

The neutral substance which remained after removing the desylacetic acid was recrystallised from a mixture of benzene and light petroleum. It was deposited in prismatic needles melting at 151.5° , and proved to be *diphenyl- Δ^1 -croto lactone*. This was confirmed by the mixture melting-point test:

0.1591 gave 0.4768 CO_2 and 0.0739 H_2O . $\text{C} = 81.73$; $\text{H} = 5.16$.

$\text{C}_{16}\text{H}_{12}\text{O}_2$ requires $\text{C} = 81.35$; $\text{H} = 5.09$ per cent.

II. β -METHYLANHYDRACETONEBENZIL,

Oxidation of β -Methylanhydracetonebenzil with Chromium Trioxide.

Ten grams of β -methylanhydracetonebenzil (m. p. 180°) in fine powder were suspended in 40 c.c. of glacial acetic acid, and a solution of 15 grams of chromium trioxide in the same solvent was added fairly rapidly, using a mechanical stirrer and cooling during the process. During the addition of the chromium trioxide the suspended substance went into solution. After standing in the cold for three days, the mixture was diluted with water, and the green precipitate was filtered off and dissolved in sodium carbonate. The alkaline solution was digested for several hours on the water bath, after which it was filtered from chromium compounds and acidified. If the acid precipitated is not quite colourless, it should be redissolved in sodium carbonate and the warming continued. A further quantity of the acid may be obtained from the original dilute acetic acid filtrate by extraction with ether. The acid was crystallised from ether, from which it separates in obliquely-terminated four-sided prisms melting at 176° with decomposition. In polarised light the crystals show an extinction angle of 22° . It is readily soluble in alcohol, acetone, and ethyl acetate, very sparingly soluble in benzene. The yield is fair,

5—6 grams of the acid being obtained from 10 grams of β -methyl-anhydracetonebenzil.

Analysis gave figures agreeing with the formula of α -methyl- α' - β -diphenyl- α' - β -dihydroxyglutaric acid,
$$\text{C}_6\text{H}_5 \cdot \text{C}(\text{OH}) \cdot \text{CO}_2\text{H} \\ \text{C}_6\text{H}_5 \cdot \text{C}(\text{OH}) \cdot \text{CH}(\text{CH}_3) \cdot \text{CO}_2\text{H}$$

0.1267 gave 0.3037 CO_2 and 0.0632 H_2O . $\text{C} = 65.36$; $\text{H} = 5.54$.

0.1369 „ 0.3274 CO_2 and 0.0698 H_2O . $\text{C} = 65.22$; $\text{H} = 5.66$.

$\text{C}_{18}\text{H}_{18}\text{O}_6$ requires $\text{C} = 65.45$; $\text{H} = 5.45$ per cent.

The silver salt was obtained as a white precipitate on adding silver nitrate to a solution of the ammonium salt.

0.2074 gave 0.3045 CO_2 , 0.0535 H_2O and 0.0829 Ag. $\text{C} = 40.04$; $\text{H} = 2.86$; $\text{Ag} = 39.97$.

$\text{C}_{18}\text{H}_{16}\text{O}_6\text{Ag}_2$ requires $\text{C} = 39.71$; $\text{H} = 2.94$; $\text{Ag} = 39.69$ per cent.

Action of Heat on Methyl-diphenyldihydroxyglutaric Acid.—A quantity of the acid was distilled under reduced pressure. The distillate, which was a pale-yellow, viscid substance, was treated with ether, which deposited it in large tabular crystals, of rhombic outline. Recrystallised from alcohol, they melted constantly at 138 — 139° . Analysis gave figures agreeing with the formula $\text{C}_{17}\text{H}_{14}\text{O}_2$.

0.1551 gave 0.4631 CO_2 and 0.0817 H_2O . $\text{C} = 81.43$; $\text{H} = 5.85$.

$\text{C}_{17}\text{H}_{14}\text{O}_2$ requires $\text{C} = 81.60$; $\text{H} = 5.60$ per cent.

By heating the acid, first at 155° and afterwards at 215° , in a Sprengel vacuum and pumping off and measuring the gas, it was found that exactly 1 mol. of carbon dioxide was eliminated. Water was also seen to be given off. The compound is formed according to the equation,

Japp and Lander showed that diphenyldihydroxyglutaric acid, when heated at 105° , yielded isocinnamethylmandelic acid according to the equation,

and that, when the isocinnamethylmandelic acid thus formed was heated at 160° , it decomposed as follows :

(Trans., 1897, 71, 134 and 139). The foregoing compound $\text{C}_{17}\text{H}_{14}\text{O}_2$ is doubtless the methyl homologue of this $\text{C}_{16}\text{H}_{12}\text{O}_2$, and the reaction

in which it is formed is a combination of the two just quoted. An attempt which we made to stop this reaction half way, so as to obtain a methyl homologue of isocinnamemylmandelic acid, led to no result.

Action of Hydriodic Acid on Methylphenyldihydroxyglutaric Acid:

Formation of Methylphenyl- Δ^1 -crotonolactone,
$$\begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{C}_6\text{H}_5 \cdot \text{CH} \quad \text{CO} \\ \text{C}_6\text{H}_5 \cdot \text{C} = \text{C} \cdot \text{CH}_3 \end{array}$$
—The acid was boiled for two minutes with fuming hydriodic acid, and the product was purified in the usual way. The compound was deposited from ether in transparent, thick crystals of rhombic outline, melting at 88.5° , and proved to be *methylphenylcrotonolactone*. It was further identified by the mixture melting-point test, and this result was confirmed by analysis.

0.1630 gave 0.4866 CO_2 and 0.0839 H_2O . $\text{C} = 81.41$; $\text{H} = 5.71$.

$\text{C}_{17}\text{H}_{14}\text{O}_2$ requires $\text{C} = 81.60$; $\text{H} = 5.60$ per cent.

As the process in which the foregoing compound is formed is not a reduction, we tried whether fuming hydrochloric acid would effect the same change as hydriodic acid. Methylphenyldihydroxyglutaric acid was therefore boiled with fuming hydrochloric acid for ten minutes; but only about 10 per cent. of it was transformed into methylphenylcrotonolactone, the remainder being recovered unchanged.

III. $\alpha\beta$ -DIMETHYLANHYDRACETONEBENZIL,

Oxidation of $\alpha\beta$ -Dimethylanhydracetonebenzil with Chromium Trioxide.

Twenty grams of finely-powdered $\alpha\beta$ -dimethylanhydracetonebenzil were suspended in 70 c.c. of glacial acetic acid, and an acetic acid solution of 30 grams of chromium trioxide was gradually added, the oxidation being carried out in the cold as in the processes already described. The substance went into solution during the addition of the chromium trioxide; but by the next day a considerable quantity of a crystalline deposit had formed. After standing for 3 days, the mixture was diluted with water, and the crystalline precipitate was filtered off and washed with water, by which means it was obtained almost white. (The filtrate contains chiefly benzoic acid and may be rejected.) The precipitate was dissolved in ether and the ethereal solution was shaken with a solution of *potassium carbonate*, which left a neutral substance dissolved in the ether. On adding to the potassium carbonate extract a solution of sodium carbonate, the sparingly soluble sodium salt of the new acid was

precipitated; it was separated by filtration and decomposed by shaking it with dilute sulphuric acid and ether in a separating funnel. The aqueous filtrate from the sodium salt yields, on acidifying, a further quantity of the acid, but contaminated with benzoic acid; the latter may be removed by extraction with boiling light petroleum. The new acid was crystallised, first from ether, and then from a mixture of acetone and light petroleum. From either solvent it separates in short six-sided prisms with pointed ends. It melts, with decomposition, at 164° .

Analysis gave figures agreeing with the formula of γ -aceto- α -methyl- $\beta\gamma$ -diphenyl- $\beta\gamma$ -oxidobutyric acid,

$$\begin{array}{c} \text{C}_6\text{H}_5 \cdot \text{C} \begin{array}{l} \diagup \text{CO} \cdot \text{CH}_3 \\ \diagdown \text{O} \end{array} \\ | \\ \text{C}_6\text{H}_5 \cdot \text{C} \begin{array}{l} \diagup \text{CH}(\text{CH}_3) \cdot \text{CO}_2\text{H} \\ \diagdown \end{array} \end{array}$$

0.1461 gave 0.3947 CO_2 and 0.0784 H_2O . $\text{C} = 73.67$; $\text{H} = 5.96$.

0.1534 „ 0.4124 CO_2 „ 0.0808 H_2O . $\text{C} = 73.32$; $\text{H} = 5.85$.

$\text{C}_{19}\text{H}_{18}\text{O}_4$ requires $\text{C} = 73.55$; $\text{H} = 5.81$ per cent.

The *silver* salt was obtained as a white powder by precipitating the ammonium salt (itself only sparingly soluble in water) with silver nitrate.

0.2902 gave 0.0741 Ag . $\text{Ag} = 25.5$.

$\text{C}_{19}\text{H}_{17}\text{O}_4\text{Ag}$ requires $\text{Ag} = 25.9$ per cent.

The *neutral substance* remaining in the ether after the removal of the acid by potassium carbonate was deposited in large flat octahedral crystals. It may also be crystallised from hot alcohol or light petroleum. Its behaviour on melting is peculiar: it melts about 89° to a semi-opaque liquid, which clears about 120° with evolution of gas.

The specimens used for analysis were crystallised (1) from alcohol, (2) from ether, (3) from light petroleum. The figures obtained agreed with the formula of 1 : 3-dimethyl-4 : 5-diphenyl-1 : 4 : 5-trihydroxycyclopentanone-(2),

0.1355 gave 0.3608 CO_2 and 0.0802 H_2O . $\text{C} = 72.63$; $\text{H} = 6.58$.

0.1640 „ 0.4364 CO_2 „ 0.0943 H_2O . $\text{C} = 72.57$; $\text{H} = 6.39$.

0.1555 „ 0.4148 CO_2 „ 0.0900 H_2O . $\text{C} = 72.75$; $\text{H} = 6.43$.

$\text{C}_{19}\text{H}_{20}\text{O}_4$ requires $\text{C} = 73.08$; $\text{H} = 6.41$ per cent.

Twenty grams of $\alpha\beta$ -dimethylanhydracetonebenzil yielded, on oxidation, 4—5 grams of the acid and 6 grams of the neutral product.

A. *Reactions of γ -Aceto- α -methyl- β - γ -diphenyl- β - γ -oxidobutyric Acid,* *Action of Phenylhydrazine: Formation of the Compound,*

—Three grams of acetomethyldiphenyloxidobutyric acid, 1 gram of phenylhydrazine, and a little alcohol were heated in a sealed tube at 100° for three hours. During the heating large crystals separated; these were filtered off, washed with alcohol and with ether, in which they were practically insoluble, and recrystallised from boiling benzene, from which the compound was deposited in colourless prisms melting, with decomposition, at 212° . It does not dissolve at 100° either in sodium hydroxide or in strong hydrochloric acid.

0.1606 gave 0.4385 CO_2 and 0.0897 H_2O . C = 74.46; H = 6.20.

0.1806 „ 11.4 c.c. moist nitrogen at 16° and 759 mm. N = 7.34.

$\text{C}_{25}\text{H}_{24}\text{O}_3\text{N}_2$ requires C = 75.00; H = 6.00; N = 7.00 per cent.

Three grams of the acid yielded 3.2 grams of the compound melting at 212° .

The foregoing compound does not act further with phenylhydrazine at 100° , whilst at 150° there is considerable decomposition, crystals of ammonium carbonate being found in the tube. The product was not further examined.

Oxime, —To 2 grams of acetomethyl-diphenyloxidobutyric acid, dissolved in an aqueous solution of 5 grams of potassium hydroxide, 1.8 grams (4 mol. proportions) of hydroxylamine hydrochloride were added, and the mixture was allowed to stand in the cold for 3 days. On acidifying the solution, a white precipitate was obtained; this was crystallised twice from a mixture of ether and light petroleum, and was thus obtained in spherical aggregates of slender needles, melting, with decomposition, at 172 — 173° . It is soluble in sodium carbonate.

Analysis showed that the *oxime* of the acid had been formed:

0.1626 gave 0.4171 CO_2 and 0.0864 H_2O . C = 69.95; H = 5.90.

0.3543 „ 13.9 c.c. moist nitrogen at 19° and 760 mm. N = 4.51.

$\text{C}_{19}\text{H}_{19}\text{O}_4\text{N}$ requires C = 70.15; H = 5.84; N = 4.30 per cent.

The silver salt was obtained as a white precipitate by adding silver nitrate to a solution of the oxime in dilute ammonia :

0.3330 gave 0.0830 Ag. $\text{Ag} = 24.92$.

$\text{C}_{19}\text{H}_{18}\text{O}_4\text{NAg}$ requires $\text{Ag} = 24.98$ per cent.

Action of Heat: Formation of β -Aceto- α -ethyl- $\alpha\beta$ -diphenyloxidoethane,
 $\text{C}_6\text{H}_5 \cdot \text{C} \begin{array}{c} \diagup \text{CO} \cdot \text{CH}_3 \\ \diagdown \text{O} \\ \diagup \text{C}_2\text{H}_5 \end{array}$
 $\text{C}_6\text{H}_5 \cdot \text{C} \begin{array}{c} \diagup \text{O} \\ \diagdown \text{C}_2\text{H}_5 \end{array}$.—A weighed quantity of acetomethyldiphenyloxido-butyric acid was heated at its melting point (164°) in a small exhausted flask, connected with a Sprengel pump, until gas ceased to be evolved. The gas was pumped off, measured, and then absorbed by potassium hydroxide. It was found to be almost pure carbon dioxide and its amount corresponded almost exactly with the elimination of 1 mol. of that gas, as did also the loss in weight of the substance taken.

The product remaining in the flask solidified, on cooling, to a colourless, crystalline mass. It was dissolved in ether and the solution was extracted with potassium carbonate and sodium hydroxide; but these removed only a trace of acid. The neutral substance remaining on evaporation of the ether was crystallised from alcohol: it formed long four-sided needles, obliquely terminated, melting constantly at $98-99^\circ$. Analysis confirmed the above results as to the nature of the decomposition :

0.1470 gave 0.4360 CO_2 and 0.0914 H_2O . $\text{C} = 80.89$; $\text{H} = 6.90$.

0.1542 „ 0.4579 CO_2 „ 0.0954 H_2O . $\text{C} = 80.98$; $\text{H} = 6.87$.

$\text{C}_{18}\text{H}_{18}\text{O}_2$ requires $\text{C} = 81.20$; $\text{H} = 6.76$ per cent.

The compound would be β -aceto- α -ethyl- $\alpha\beta$ -diphenyloxidoethane, assuming that, in the reaction in which it is formed, the elimination of carbon dioxide is not accompanied by any migration.

The mother liquor from this compound deposited a small quantity of rhombic prisms, which, without purification, melted at $114-115^\circ$. The quantity was insufficient for further examination.

The semicarbazone, $\text{C}_6\text{H}_5 \cdot \text{C} \begin{array}{c} \diagup \text{C}(\text{N} \cdot \text{NH} \cdot \text{CO} \cdot \text{NH}_2) \cdot \text{CH}_3 \\ \diagdown \text{O} \\ \diagup \text{C}_2\text{H}_5 \end{array}$, of acetoethyl-

diphenyloxidoethane, was prepared by the method already described. It crystallised from alcohol in lustrous, small, thin plates melting at 204° .

0.1230 gave 13.7 c.c. moist nitrogen at 10° and 752 mm. $\text{N} = 13.19$.

$\text{C}_{19}\text{H}_{21}\text{O}_2\text{N}_3$ requires $\text{N} = 13.00$ per cent.

Oxidation with Potassium Hypobromite: Formation of Methyl-diphenyl-dihydroxyglutaric Acid,
 $\text{C}_6\text{H}_5 \cdot \text{C}(\text{OH}) \cdot \text{CO}_2\text{H}$
 $\text{C}_6\text{H}_5 \cdot \text{C}(\text{OH}) \cdot \text{CH}(\text{CH}_3) \cdot \text{CO}_2\text{H}$.—Three grams

of acetomethyldiphenyloxidobutyric acid were added to a solution of potassium carbonate. The sparingly soluble potassium salt separated.* The mixture was gently warmed on the water-bath, and a solution of potassium hypobromite (prepared by dissolving 6 grams of bromine in a solution of 7 grams of potassium hydroxide in 30 c.c. of water) was gradually added, the warming being continued for half-an-hour. The potassium salt went into solution, and a strong smell of bromoform was noticeable, whilst a small quantity of a heavy liquid separated; the latter crystallised on cooling, but the quantity was insufficient for examination. The filtered solution was treated with sulphur dioxide and acidified. The acid, thus precipitated, was recrystallised from a mixture of ether and ligroin, and showed all the properties of *methyldiphenyldihydroxyglutaric acid*, a compound already obtained by the oxidation of β -methylanthracetonebenzil (*v. supra*). Like this substance it forms obliquely-terminated, four-sided prisms, with an extinction angle of 22° in polarised light, and melts, with decomposition, at 176° . Mixed with a sample of the acid prepared from β -methylanthracetonebenzil, it showed no depression of melting point. Analysis gave confirmatory results.

0.1652 gave 0.3972 CO_2 and 0.0846 H_2O . C = 65.57; H = 5.69.

0.1631 „ 0.3906 CO_2 „ 0.0829 H_2O . C = 65.31; H = 5.64.

$\text{C}_{18}\text{H}_{18}\text{O}_6$ requires C = 65.45; H = 5.45 per cent.

The yield is very good.

By conducting the foregoing oxidation in the cold, a complex mixture of acids was obtained, one of which, at least, contained bromine. These products were not further examined.

Action of Hydriodic Acid: Formation of Methyldiphenyl- Δ^1 -croto-

lactone, .—Four grams of acetomethyldiphenyloxido-

butyric acid were boiled with excess of fuming hydriodic acid for 3 minutes. The product was washed with water, dissolved in ether, and treated with sulphurous acid and potassium carbonate solution. The latter extracted only a small quantity of an acid which crystallised from ether in thin, rectangular plates melting about 170° with decomposition; there was not sufficient for further examination. The neutral substance remaining in the ether was deposited in clear, thick crystals, of rhombic outline; they melted at 88.5° and proved to be *methyldiphenyl- Δ^1 -croto-lactone*, a substance already obtained in other reactions in the course of the present work. Their identity was further established

* It would doubtless have been better to have used the readily soluble sodium salt, and to have oxidised with sodium hypobromite.

by the mixture melting-point method, a specimen of the synthetic compound (from α -desylpropionic acid, *v. infra*) being employed for comparison, and also by analysis.

0.1575 gave 0.4721 CO_2 and 0.0817 H_2O . $\text{C} = 81.74$; $\text{H} = 5.76$.

$\text{C}_{17}\text{H}_{14}\text{O}_2$ requires $\text{C} = 81.60$; $\text{H} = 5.60$ per cent.

The yield was about 2 grams.

In order to obtain the corresponding acid, the lactone was warmed with alcoholic potassium hydroxide. The acid, liberated from its salt, crystallised from alcohol in flat needles melting, with decomposition, at 220° . It proved to be identical with Knöevenagel's α -desylpropionic

acid, $\text{C}_6\text{H}_5 \cdot \text{CO} \cdot \text{C}_6\text{H}_5 \cdot \text{CH} \cdot \text{CH}(\text{CH}_3) \cdot \text{CO}_2\text{H}$, which this investigator prepared by acting with ethyl α -bromopropionate on sodium deoxybenzoin, and hydrolysing the ester thus obtained (*Ber.*, 1888, 21, 1353). Knöevenagel gives the melting point of his acid as $213-215^\circ$; but a specimen, which we prepared by his method, melted, as above, at 220° , and, when mixed with the acid from the lactone, showed no depression of melting point. Much, however, depends upon the rate of heating, as, in the neighbourhood of its melting point, the acid is gradually transformed into the lactone, and shows signs of softening even as low as 200° .

The acid prepared from the lactone gave figures agreeing with the formula of α -desylpropionic acid.

0.1600 gave 0.4444 CO_2 and 0.0886 H_2O . $\text{C} = 75.75$; $\text{H} = 6.15$.

$\text{C}_{17}\text{H}_{16}\text{O}_3$ requires $\text{C} = 76.11$; $\text{H} = 5.97$ per cent.

A specimen of α -desylpropionic acid prepared by Knöevenagel's method was distilled under reduced pressure. The temperature of the bath was slowly raised to $255-260^\circ$, when the substance passed over. The distillate was dissolved in ether, and the solution deposited clear thick rhombs of *methyldiphenyl- Δ^1 -crotonolactone* melting at 88.5° . As already mentioned, the melting point was not depressed when the substance was mixed with the lactone prepared by the action of hydriodic acid on acetomethyldiphenyloxidobutyric acid.

If α -desylpropionic acid were treated in the cold with acetic anhydride containing a few drops of sulphuric acid, it ought to yield the labile *methyldiphenyl- Δ^2 -crotonolactone* (not yet prepared); but we did not try this experiment as we wished to avoid trenching on Thiele's work in this field.

Action of Acetic Anhydride: Formation of the Lactone,

(*m. p.* 140°).—Four grams of acetomethyldiphenyloxidobutyric acid

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were added to 32 c.c. of acetic anhydride with which 8 drops of concentrated sulphuric acid had previously been mixed. The substance readily dissolved. After standing for a day at ordinary temperature, the mixture was poured into excess of water. The precipitate was filtered off and dissolved in ether. Potassium carbonate removed only a trace of acid. On evaporation of the ether, the neutral substance, which proved to be an *acetoxylactone* of the formula above given, was deposited in short, four- or six-sided prisms. Recrystallised from a mixture of benzene and ligroin, it melted constantly at 140° . The yield was about 1 gram.

0.1606 gave 0.4216 CO_2 and 0.0828 H_2O . $\text{C} = 71.59$; $\text{H} = 5.72$.

0.1596 „ 0.4173 CO_2 „ 0.0827 H_2O . $\text{C} = 71.30$; $\text{H} = 5.75$.

$\text{C}_{21}\text{H}_{20}\text{O}_5$ requires $\text{C} = 71.59$; $\text{H} = 5.68$ per cent.

The foregoing compound, when warmed with alcoholic potassium hydroxide, yielded *α -desylpropionic acid* (m. p. 220° , with decomposition), which was identified by its properties, by the mixture melting-point test, and by analysis.

0.1570 gave 0.4403 CO_2 and 0.0859 H_2O . $\text{C} = 76.48$; $\text{H} = 6.07$.

$\text{C}_{17}\text{H}_{16}\text{O}_3$ requires $\text{C} = 76.11$; $\text{H} = 5.97$ per cent.

B. *Reactions of 1:3-Dimethyl-4:5-diphenyl-1:4:5-trihydroxycyclopentanone-(2),*

Semicarbazone.—The *semicarbazone* of dimethyldiphenyltrihydroxycyclopentanone, the neutral oxidation product of *$\alpha\beta$ -dimethylanhydracetonebenzil*, was prepared in the cold by the method already described. It crystallised from alcohol in slender needles, melting very indefinitely between 165° and 180° with decomposition.

0.1589 gave 16.2 c.c. moist nitrogen at 16° and 748 mm. $\text{N} = 11.69$.

$\text{C}_{20}\text{H}_{23}\text{O}_4\text{N}_3$ requires $\text{N} = 11.38$ per cent.

Action of Hydroxylamine.—An alcoholic solution of 1 gram of dimethyldiphenyltrihydroxycyclopentanone was mixed with a concentrated aqueous solution of 0.66 gram (3 mols.) of hydroxylamine hydrochloride, and 0.5 gram of finely powdered anhydrous sodium carbonate was added. The mixture was allowed to stand for 9 days in the cold. The solution was then filtered from the precipitate of sodium chloride and diluted with water until a turbidity was produced. On standing, the liquid deposited crystals of a substance which, after recrystallisation from a mixture of ether and light petroleum, was

obtained in laminae of rhombic outline, melting with decomposition at 185°.

Analysis gave figures pointing to the formula $C_{19}H_{24}O_5N_2$.

0.1910 gave 0.4400 CO_2 and 0.1159 H_2O . $C = 62.82$; $H = 6.74$.

0.2208 gave 14.8 c.c. moist nitrogen at 15° and 752 mm. $N = 7.76$.

$C_{19}H_{24}O_5N_2$ requires $C = 63.33$; $H = 6.66$; $N = 7.77$ per cent.

The compound is formed according to the equation

only one mol. of water being eliminated. Probably the *cyclopentane* ring opens in the process; but, even then, it is difficult to reconcile the constitution of a dimethyldiphenyltrihydroxycyclopentanone, which we ascribe to the compound $C_{19}H_{20}O_4$, with the formation of this hydroxylamine derivative.

The foregoing experiment was repeated, substituting potassium acetate for sodium carbonate, but only an uncrystallisable gum was obtained.

Attempt to Oxidise Dimethyldiphenyltrihydroxycyclopentanone by means of Chromium Trioxide to Acetomethyldiphenyloxidobutyric Acid.—We record this negative result because it is of importance as showing that dimethyldiphenyltrihydroxycyclopentanone is not an intermediate product in the oxidation of $\alpha\beta$ -dimethylanhydracetonebenzil to acetomethyldiphenyloxidobutyric acid (*v. supra*).

The *cyclopentanone* derivative and the chromium trioxide, dissolved in glacial acetic acid, were in one case allowed to stand in the cold for a fortnight and, in another, warmed on the water-bath for 10 minutes. In the first case there was no action at all; in the second, a little benzoic acid was formed, but the greater part of the *cyclopentanone* derivative was recovered unchanged.

Action of Hydriodic Acid.—Five grams of dimethyldiphenyltri-hydroxycyclopentanone were boiled with excess of fuming hydriodic acid for 2 minutes. The product was dissolved in ether and successively treated with sulphurous acid and sodium carbonate solution. The latter removed an acid—the chief product of the reaction—which crystallised from alcohol in flat, lustrous, prismatic needles melting at 215–216°. (Yield: 2.6 grams.)

Analysis gave figures agreeing with the formula $C_{19}H_{18}O_2$.

0.1605 gave 0.4801 CO_2 and 0.0974 H_2O . $C = 81.58$; $H = 6.74$.

0.1472 gave 0.4406 CO_2 and 0.0884 H_2O . $C = 81.63$; $H = 6.67$.

$C_{19}H_{18}O_2$ requires $C = 82.01$; $H = 6.47$ per cent.

The acid is formed according to the equation

The *silver* salt was obtained as a white precipitate by adding silver nitrate to the ammonium salt.

0.4611 gave 0.1268 Ag. $\text{Ag} = 27.49$.

$\text{C}_{19}\text{H}_{17}\text{O}_2$ Ag requires $\text{Ag} = 28.02$ per cent.

A solution of the acid in sodium carbonate is stable towards permanganate in the cold.

A solution of the acid in glacial acetic acid decolorised a solution of bromine in the same solvent. The weight of the additive compound obtained from 2 grams of acid was 3 grams, showing that a *dibromide* had been formed. The dibromide, recrystallised from a mixture of ether and light petroleum, melted, with decomposition, at 114° ; but as it turned yellow when we attempted to purify it, and was evidently decomposing, we did not attempt to analyse it.

On warming a solution of the acid in potassium carbonate with potassium hypobromite, a small quantity of an uncrystallisable neutral compound was formed; but the greater part of the acid was recovered unchanged.

Sodium in boiling alcohol is without action on the acid; neither did boiling for 4 hours with hydriodic acid and amorphous phosphorus alter it. By heating it however with this mixture at 150° for 8 hours, a neutral substance and an acid were obtained, neither of which, however, could be induced to crystallise.

The formula of an acid, $\text{C}_{19}\text{H}_{18}\text{O}_2$, formed from dimethyldiphenyl-trihydroxycyclopentanone, may be resolved into

If the unresolved group C_4 is an open chain, it must contain either one set of triple bonds, or two sets of double bonds, neither of which constitutions would be in harmony with the stability of the acid towards both reducing and oxidising agents, especially towards permanganate. It is more probable, therefore, that this C_4 is a cyclobutene group; and, on this assumption, a possible constitution for

the acid would be $\begin{array}{c} \text{C}_6\text{H}_5 \cdot \text{C} - \text{C}(\text{CH}_3) \cdot \text{CO}_2\text{H} \\ | \quad | \\ \text{C}_6\text{H}_5 \cdot \text{C} - \text{CH} \cdot \text{CH}_3 \end{array}$. It would be necessary to

assume that the pentacarbon ring of dimethyldiphenyltrihydroxycyclopentanone opens, and then closes again, forming a tetracarbon ring. The formula would account for the stability of the acid towards permanganate, as there is no hydrogen attached to the doubly-linked carbon atoms (compare Trans., 1897, 71, 129), and also for the formation of a dibromide.

The original ethereal solution of the crude reduction product, from which the foregoing acid had been removed by sodium carbonate, left, on evaporation, a crystalline residue, which, by treatment with alcohol, was separated into the two following substances:

1. Needles (0.3 gram), melting at 175° and showing straight extinction in polarised light. On attempting to recrystallise the substance from alcohol, benzene, or ether, it was deposited in a pulverulent form. It appears to be identical with the compound $C_{19}H_{16}O_2$ (m. p. 178°) obtained by the action of acetic anhydride, with the addition of a few drops of sulphuric acid, on dimethyldiphenyltrihydroxycyclopentanone (*v. infra*). Mixed with a little of the compound $C_{19}H_{16}O_2$, it still melted at 175° . The low melting point of the present preparation is due to the fact that there was not sufficient substance for complete purification.

2. Four-, six-, or eight-sided laminae (0.6 gram), which, on recrystallisation, melted at 122° . This substance was proved, by the mixture melting-point test, to be identical with *dimethyldiphenylcyclopentenone*, $\begin{matrix} C_6H_5 \cdot C \cdot CH(CH_3) \\ | \\ C_6H_5 \cdot C \cdot CH(CH_3) \end{matrix} > CO$ (obtained by the reduction of $\alpha\beta$ -dimethylanhydracetonebenzil with hydriodic acid, and to be described, along with its derivatives, in a subsequent communication). Analysis confirmed this result.

0.1559 gave 0.4953 CO_2 and 0.0969 H_2O . C = 86.64; H = 6.90.

$C_{19}H_{18}O$ requires C = 87.02; H = 6.87 per cent.

Action of Acetic Anhydride.—Five grams of finely powdered dimethyldiphenyltrihydroxycyclopentanone were added to a mixture of 8 c.c. of acetic anhydride and 2 drops of concentrated sulphuric acid. The substance rapidly dissolved, the temperature rising and the solution becoming dark-coloured. On standing, the solution deposited thick prisms; the liquid was poured off from the crystals and mixed with water. Both the crystals and the precipitated solid yielded, on recrystallisation from alcohol, long needles showing straight extinction in polarised light and melting at 178° . The substance usually crystallises well from alcohol, ether, benzene or light petroleum, but is sometimes deposited in a pulverulent form. (Yield 2.9 grams.)

0.1640 gave 0.4976 CO_2 and 0.0878 H_2O . C = 82.74; H = 5.94.

0.1569 „ 0.4758 CO_2 „ 0.0834 H_2O . C = 82.70; H = 5.90.

$C_{19}H_{16}O_2$ requires C = 82.61; H = 5.80 per cent.

Warmed with alcoholic potassium hydroxide, the foregoing compound yields an acid; but the yield is very poor, and the chief product is a dark-coloured amorphous mass. The reaction was not further studied.

Action of Potassium Hydroxide.—Five grams of dimethyldiphenyltrihydroxycyclopentanone were dissolved in 50 c.c. of cold 5 per cent. alcoholic potassium hydroxide, and the solution, which was yellow, was allowed to remain at the ordinary temperature for 20 minutes,

after which it was diluted with water. The solution, which remained clear, was then saturated with carbon dioxide; this precipitated a viscid substance which was removed with ether; and the remaining aqueous solution gave, on acidifying with hydrochloric acid, no further precipitate. The ethereal solution, when concentrated, deposited a solid substance; this was powdered, filtered, and washed with a mixture of ether and light petroleum to remove oil and a pink colouring matter; and the residue, which weighed 4 grams, was recrystallised from methyl alcohol. It crystallised in colourless, large, flat, six-sided prisms, usually hollow; also in large tabular crystals like flat octahedra. Both forms melted at $89-90^{\circ}$. Analysis showed that the substance had the formula $C_{19}H_{18}O_3$, having been formed from dimethyldiphenyltrihydroxycyclopentanone by abstraction of a molecule of water.

0.1563 gave 0.4428 CO_2 and 0.0864 H_2O . $C = 77.26$; $H = 6.14$.

$C_{19}H_{18}O_3$ requires $C = 77.55$; $H = 6.12$ per cent.

By allowing the solution of dimethyldiphenyltrihydroxycyclopentanone in alcoholic potassium hydroxide to remain for several days, and then evaporating off the alcohol in a vacuum desiccator over sulphuric acid, the compound $C_{19}H_{18}O_3$ (m.p. $89-90^{\circ}$), which is formed in the first instance, is decomposed, and ethyl phenyl ketone and potassium benzoate are obtained in its place. This decomposition is, however, better effected with the aid of boiling aqueous potassium hydroxide (*v. infra*).

By oxidising the compound $C_{19}H_{18}O_3$ (m.p. $89-90^{\circ}$), with chromium trioxide in acetic acid solution, benzoic acid and an oil smelling of ethyl phenyl ketone were also obtained.

One gram of the compound $C_{19}H_{18}O_3$ (m.p. $89-90^{\circ}$) was boiled with fuming hydriodic acid for 5 minutes. The product, treated in the usual way, yielded a compound crystallising from ether or alcohol in oblique tables, usually with one of the corners truncated, melting at 144.5° . It is not affected by alcoholic potassium hydroxide even when heated with it on the water-bath for 4 hours. Analysis showed that it had been formed according to the equation

the hydriodic acid having had a dehydrating, not a reducing, action.

0.1586 gave 0.4791 CO_2 and 0.0830 H_2O . $C = 82.38$; $H = 5.81$.

0.1585 „ 0.4793 CO_2 „ 0.0832 H_2O . $C = 82.47$; $H = 5.83$.

$C_{19}H_{16}O_2$ requires $C = 82.61$; $H = 5.80$ per cent.

In order to study the more exhaustive action of potassium hydroxide on dimethyldiphenyltrihydroxycyclopentanone, 6 grams of this substance were heated in a distilling flask with a dilute aqueous solution of 6 grams of potassium hydroxide. Drops of a clear oil passed over with the aqueous distillate. As soon as the oil ceased to distil over, the process was interrupted. The solution remaining in the distilling flask contained a crystalline matter in suspension; this was collected and purified by recrystallisation, first from a mixture of benzene and light petroleum, afterwards from alcohol. It formed oblique tables, sometimes with the acute corners truncated, and melted at 144.5° . It was identical with the compound $C_{19}H_{16}O_2$, just described, as was proved both by the mixture melting-point test and by analysis.

0.1789 gave 0.5387 CO_2 and 0.0952 H_2O . $C = 82.12$; $H = 5.91$.

$C_{19}H_{16}O_2$ requires $C = 82.61$; $H = 5.80$.

The yield of this substance was small.

On acidifying the alkaline filtrate a considerable quantity of *benzoic acid* was precipitated.

The oil, above referred to, was extracted from the aqueous distillate with ether, the ethereal solution was dried with calcium chloride, and, after expelling the ether, the oil was distilled under reduced pressure. It proved to be *ethyl phenyl ketone*. Placed in a refrigerator it solidified to a mass of crystals which melted at 17° . A specimen of ethyl phenyl ketone, obtained from Kahlbaum and further purified by distillation under reduced pressure, was cooled with water and then touched with a crystal of the foregoing substance. It crystallised instantly, and the crystals melted at 18° . A mixture of the two specimens melted also at 18° . Analysis of the substance obtained in the present reaction gave figures agreeing with the formula of ethyl phenyl ketone.

0.1710 gave 0.5047 CO_2 and 0.1158 H_2O . $C = 80.49$; $H = 7.52$.

$C_9H_{10}O$ requires $C = 80.60$; $H = 7.46$.

In the action of hot aqueous potassium hydroxide on dimethyldiphenyltrihydroxycyclopentanone there are evidently two reactions: one in which the compound $C_{19}H_{16}O_2$ is formed from the whole molecule by abstraction of two mols. of water, this compound, when once formed, being quite stable towards potassium hydroxide; and another in which the molecule of the original substance is broken up, yielding benzoic acid and ethyl phenyl ketone. It is probable that one of the primary products of hydrolysis is α -benzoylpropionic acid $C_6H_5 \cdot CO \cdot CH(CH_3) \cdot CO_2H$, as may be seen by inspection of the constitutional formula of dimethyldiphenyltrihydroxycyclopentanone; and

that this β -ketonic acid then parts with carbon dioxide, yielding ethyl phenyl ketone; but even α -benzoylpropionic acid and benzoic acid together would not account for more than 17 out of the 19 carbon atoms of the original compound. We were, however, unable to discover any further product of decomposition.

IV. $\beta\beta$ -DIMETHYLANHYDRACETONEBENZIL,

Oxidation of $\beta\beta$ -Dimethylanhhydracetonebenzil with Chromium Trioxide.

Twenty grams of finely powdered $\beta\beta$ -dimethylanhhydracetonebenzil were suspended in 70 c.c. of glacial acetic acid, and a solution of 30 grams of chromium trioxide in the same solvent was gradually added, the mixture being cooled with water during the process. The suspended substance went into solution during the addition of the chromium trioxide; but in the course of a few hours a large quantity of a crystalline deposit had formed. After standing overnight the mixture was filtered, and the solid was washed, first with glacial acetic acid and then with water. The product is almost white. A further quantity can be obtained by precipitating the acetic acid filtrate with water and extracting with ether. The substance obtained by these processes was dissolved in potassium carbonate, and the solution was filtered from unaltered substance. The filtrate was then warmed for several hours on the water-bath, filtered from chromium compounds, and acidified. The precipitated acid was purified by recrystallisation from a mixture of ethyl acetate and light petroleum, from which it is deposited in sheaves of slender needles. (Yield 13–14 grams.) The acid appears to be dimorphous: when freshly crystallised it melts with decomposition at 171° ; but after the substance has stood for several weeks, the melting point is found to have risen to 184° . Analysis gave figures agreeing with the formula of $\alpha\alpha$ -dimethyl- $\alpha'\beta$ -diphenyl-

0.1620 gave 0.4147 CO_2 and 0.0824 H_2O . C = 69.81; H = 5.65.

0.1581 „ 0.4044 CO_2 „ 0.0802 H_2O . C = 69.76; H = 5.63.

$\text{C}_{19}\text{H}_{18}\text{O}_5$ requires C = 69.93; H = 5.52 per cent.

For analysis it was found necessary to recrystallise the acid repeatedly from the mixture of ethyl acetate and light petroleum, otherwise the value for carbon was found too low.

The *silver* salt was obtained as a white precipitate on adding silver nitrate to a solution of the ammonium salt.

0.3931 gave 0.1561 Ag. $\text{Ag} = 39.70$.

$\text{C}_{19}\text{H}_{16}\text{O}_5\text{Ag}_2$ requires $\text{Ag} = 39.98$ per cent.

Both the potassium and the sodium salts are sparingly soluble in water.

The acid is fairly stable towards oxidising agents: thus its solution in sodium carbonate is not altered by warming it either with potassium permanganate, or with potassium hypobromite. Warming with a solution of chromium trioxide in acetic acid converts it, however, into a neutral compound, crystallising from a mixture of ether and light petroleum in needles melting at $99-100^\circ$, which has not yet been further investigated.

Action of Phenylhydrazine on Dimethyldiphenyloxidoglutaric Acid:

Formation of the Compound $\text{NH} \begin{array}{c} \text{CO} \text{---} \text{C}(\text{C}_6\text{H}_5) \cdot \text{O} \cdot \text{CO} \\ \diagup \quad \diagdown \\ \text{N}(\text{C}_6\text{H}_5) \cdot \text{C}(\text{C}_6\text{H}_5) \text{---} \text{C}(\text{CH}_3)_2 \end{array}$

1.8 grams of the acid were dissolved in a little alcohol and heated in a sealed tube at 100° for 3 hours with 0.8 gram phenylhydrazine. On cooling, colourless plates (1 gram) separated, and a further quantity was obtained from the mother liquor on acidifying with acetic acid and diluting with water. The compound crystallises from ether or alcohol in large, colourless, six- or eight-sided plates, melting, without decomposition, at 182° . Analysis gave figures agreeing with the formula $\text{C}_{25}\text{H}_{22}\text{O}_3\text{N}_2$.

0.1559 gave 0.4300 CO_2 and 0.0776 H_2O . $\text{C} = 75.22$; $\text{H} = 5.53$.

0.1849 „ 11.6 c.c. moist nitrogen at 16° and 757 mm. $\text{N} = 7.28$.

$\text{C}_{25}\text{H}_{22}\text{O}_3\text{N}_2$ requires $\text{C} = 75.37$; $\text{H} = 5.52$; $\text{N} = 7.03$ per cent.

The compound is insoluble in sodium carbonate, but if evaporated to dryness with alcoholic potassium hydroxide, it forms a salt which is soluble in water. The acid, when freshly precipitated from this salt by dilute sulphuric acid, is soluble in sodium carbonate; but, on drying, it becomes insoluble in the carbonate solution, and, when recrystallised from alcohol, is converted into the plates or laminae of the foregoing compound $\text{C}_{25}\text{H}_{22}\text{O}_3\text{N}_2$, melting at 182° . The substance was further identified by the mixture melting-point test.

The γ -lactone ring thus opens under the influence of the caustic alkali, and a salt of the corresponding acid is formed; but the liberated acid is unstable and readily passes back into the lactone.

Action of Heat on Dimethyldiphenyloxidoglutaric Acid: Formation

of its Anhydride, $\begin{array}{c} \text{C}_6\text{H}_5 \cdot \text{C} \text{---} \text{CO} \\ \diagup \quad \diagdown \\ \text{C}_6\text{H}_5 \cdot \text{C} \text{---} \text{C}(\text{CH}_3)_2 \cdot \text{CO} \end{array} \text{O}$.—In order to ascertain the

nature of the decomposition which dimethyldiphenyloxidoglutaric acid underwent when heated, 2 grams of the substance were distilled at a pressure of about 12 mm. When the temperature of the oil-bath was 230—240°, the product of the action of heat distilled over, solidifying in the receiver. By recrystallisation from a mixture of benzene and light petroleum it was obtained in slender needles melting at 158°. Analysis showed that it had been formed from the acid by abstraction of a molecule of water :

0.1536 gave 0.4160 CO₂ and 0.0731 H₂O. C = 73.86 ; H = 5.28.

0.1645 „ 0.4446 CO₂ „ 0.0774 H₂O. C = 73.71 ; H = 5.22.

C₁₉H₁₆O₄ requires C = 74.02 ; H = 5.19 per cent.

It is insoluble in hot aqueous sodium hydroxide ; but, by evaporating its solution in alcoholic potassium hydroxide to dryness, a residue was obtained which dissolved completely in water. On acidifying the solution, *dimethyldiphenyloxidoglutaric acid* was obtained, which was identified both by its physical properties and by the mixture melting-point test. The compound C₁₉H₁₆O₄ is therefore, as above formulated, the *anhydride* of this acid.

Action of Acetic Anhydride on Dimethyldiphenyloxidoglutaric Acid : Formation of Dimethyldiphenyloxidoglutaric Anhydride.—One gram of the acid was dissolved in the cold in 15 c.c. of acetic anhydride to which 4 drops of concentrated sulphuric acid had been added. In a short time hair-like needles separated, which melted at 158°. The mother liquor, on dilution with water, gave a precipitate of the same substance, which, after crystallisation from a mixture of benzene and light petroleum, showed the same melting point. It was identical with the foregoing *anhydride* obtained by the action of heat on the acid, as was further proved by the mixture melting-point test.

Action of Hot Dilute Sulphuric Acid on Dimethyldiphenyloxidoglutaric Acid : Formation of Dimethyldiphenyloxidoglutaric Anhydride, α-Desyl-

isobutyric Acid, $\text{C}_6\text{H}_5 \cdot \text{C}(\text{CO}) \cdot \text{CH} \cdot \text{C}(\text{CH}_3)_2 \cdot \text{CO}_2\text{H}$, and 1:1-Dimethyl-2:3-di-

phenyl- Δ^2 -crotonolactone, $\begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{C}_6\text{H}_5 \cdot \text{C} \quad \text{CO} \\ | \quad | \\ \text{C}_6\text{H}_5 \cdot \text{C} \quad \text{C}(\text{CH}_3)_2 \end{array}$.—One gram of dimethyl-

diphenyloxidoglutaric acid was boiled for an hour with dilute sulphuric acid (1:1). On dissolving the product in ether and extracting with sodium carbonate, a small quantity of an acid was obtained, which, after crystallisation from alcohol, melted at 218° with decomposition. (It was afterwards shown to be *α-desylisobutyric acid*.) The neutral part was dissolved in benzene, and light petroleum was added : slender

needles were deposited, melting at 158° (*dimethyldiphenyloxidoglutaric anhydride*). The mother liquor yielded rhombs melting at 105 – 106° .

Five grams of dimethyloxidoglutaric acid were then boiled with dilute sulphuric acid (1:1) for 6 hours. This time none of the anhydride was obtained: the product yielded 0.2 grams of α -desylisobutyric acid (m. p. 218°) and 3.5 grams of the neutral compound crystallising in rhombs (m. p. 105 – 106°). The latter substance crystallises well from alcohol, or from a mixture of benzene and light petroleum. On analysis it gave figures agreeing with those required for *dimethyldiphenylcrotonolactone*:

0.1582 gave 0.4746 CO_2 and 0.0873 H_2O . C = 81.81; H = 6.13.

$\text{C}_{18}\text{H}_{16}\text{O}_2$ requires C = 81.81; H = 6.06 per cent.

Action of Alcoholic Potassium Hydroxide on Dimethyldiphenylcrotonolactone: Formation of α -Desylisobutyric Acid.—Two grams of the foregoing dimethyldiphenylcrotonolactone (m. p. 105 – 106°) were heated on the water-bath with excess of 5 per cent. alcoholic potassium hydroxide until the alcohol was expelled. The residue dissolved completely in water, and, on acidifying, an acid was obtained which, after recrystallisation from alcohol, formed flat needles melting at 218° with decomposition. It was identical with the acid of the same melting point obtained in small quantity by boiling dimethyldiphenyloxidoglutaric acid with dilute sulphuric acid. Analysis showed that, in the present reaction, it had been formed from dimethyldiphenylcrotonolactone by assumption of the elements of a molecule of water. It thus has the composition of *α -desylisobutyric acid*.

0.1555 gave 0.4349 CO_2 and 0.0918 H_2O . C = 76.27; H = 6.55.

$\text{C}_{18}\text{H}_{18}\text{O}_3$ requires C = 76.59; H = 6.38 per cent.

As the acid did not dissolve well in dilute ammonia, it was boiled with a solution of sodium carbonate, keeping the acid in excess. On adding silver nitrate to the filtered solution the *silver* salt was obtained as a white precipitate.

0.4901 gave 0.1352 Ag. Ag = 27.58.

$\text{C}_{18}\text{H}_{17}\text{O}_3$ Ag requires Ag = 27.75 per cent.

Synthesis of α -Desylisobutyric Acid.—In order to prove conclusively that the foregoing acid had the constitution here assigned to it, it was synthesised by the following reaction—an application of Knoevenagel's process, already referred to, for the preparation of desyl-fatty acids.

1.2 grams of sodium were dissolved in 12 grams of absolute alcohol. The solution of the ethoxide solidified on cooling. Ten

grams of deoxybenzoin were then added, which caused the mixture to liquefy. The flask was then cooled with ice, and 10 grams of ethyl α -bromoisobutyrate were gradually added. The mixture was allowed to stand for 3 hours in the cold, after which it was heated on the water-bath for a few minutes, employing a reflux condenser. Excess of 10—15 per cent. aqueous potassium hydroxide was then added, and the heating was continued for 2 hours, so as to hydrolyse the new ester. When cool, the mixture was diluted with water and extracted with ether: this removed 3 grams of unchanged deoxybenzoin. The aqueous solution was acidified, and the oily precipitate was separated and dissolved in ammonia. The filtered ammoniacal solution, on acidifying, gave a semi-solid precipitate; by recrystallisation from alcohol the substance was obtained in flat needles melting, with decomposition, at 218° . It agreed in all its physical properties with the acid obtained by boiling dimethyldiphenyloxidoglutaric acid with dilute sulphuric acid and by the action of potassium hydroxide on dimethyldiphenylcrotonolactone, and the identity was further proved by the mixture melting-point test. From its formation in the present reaction it can only be α -desylisobutyric acid,

Analysis gave figures agreeing with this formula.

0.1595 gave 0.4474 CO_2 and 0.0919 H_2O . $\text{C} = 76.50$; $\text{H} = 6.40$.

$\text{C}_{18}\text{H}_{18}\text{O}_3$ requires $\text{C} = 76.59$; $\text{H} = 6.38$ per cent.

The yield of pure substance was only 1.5 grams.

Conversion of α -Desylisobutyric Acid into Dimethyldiphenylcrotonolactone.—0.3 gram of the acid, obtained by hydrolysis of dimethyldiphenylcrotonolactone with potassium hydroxide, was dissolved in the cold in 2.5 c.c. of acetic anhydride containing 1 drop of concentrated sulphuric acid, and the mixture was allowed to stand for 24 hours. It was then poured into water, and the crystalline precipitate was separated by filtration and dissolved in ether. No acid could be extracted from the ethereal solution by sodium carbonate. The neutral substance crystallised in rhombs melting at 105 — 106° , and was identical with the dimethyldiphenylcrotonolactone obtained as already described from dimethyldiphenyloxidoglutaric acid, a result which was confirmed by the mixture melting-point test.

0.1588 gave 0.4762 CO_2 and 0.0880 H_2O . $\text{C} = 81.78$; $\text{H} = 6.15$.

$\text{C}_{18}\text{H}_{16}\text{O}_2$ requires $\text{C} = 81.81$; $\text{H} = 6.06$ per cent.

Action of Hydriodic Acid on Dimethyldiphenyloxidoglutaric Acid.—Two grams of dimethyldiphenyloxidoglutaric acid were boiled for 2

minutes with excess of fuming hydriodic acid. The product was dissolved in ether, and the solution was treated with sulphurous acid and extracted with sodium carbonate solution. This removed 1 gram of a mixture of acids, which was separated by crystallisation into unchanged acid and *α-desylisobutyric acid* (m. p. 218°). The latter gave, on analysis, figures agreeing with the formula.

0.1581 gave 0.4419 CO₂ and 0.0910 H₂O. C = 76.22 ; H = 6.39.

C₁₈H₁₈O₃ requires C = 76.59 ; H = 6.38 per cent.

The neutral portion of the product, remaining on evaporation of the ethereal solution, was crystallised from alcohol. It yielded flat prisms melting at 106° (see the following experiment) and a small quantity of lustrous, six- or eight-sided laminæ melting at 96°. We were unable to identify the latter substance.

In a second experiment a mixture of 5 grams of dimethyldiphenyl-oxidoglutaric acid, 75 grams of hydriodic acid (sp. gr. 1.7), and 5 grams of red phosphorus, was boiled for 3 hours, using a reflux condenser. The organic product was treated as in the foregoing experiment. Sodium carbonate extracted from the ethereal solution an acid which was deposited from alcohol in short prisms melting at 172° (yield: 0.35 gram) and which was subsequently shown to be *aa-dimethyl-βγ-diphenylbutyric acid*, C₆H₅·CH₂·CH(C₆H₅)·C(CH₃)₂·CO₂H (*v. infra*) ; but neither unchanged acid, nor *α-desylisobutyric acid* was observed. The ethereal solution, thus freed from acids, deposited, by spontaneous evaporation, short, flat, six-sided prisms melting at 106° (see preceding experiment). The yield of this substance was 2.8 grams. Recrystallised from alcohol, it exhibited dimorphism. From alcoholic solutions of the impure substance it separated in needles melting at 110°, but from pure solutions in the above form melting at 106°. If a supersaturated solution of the pure substance is seeded with the needles, both forms are deposited. The substance is the *lactone of*

aa-dimethyl-βγ-diphenyl-γ-hydroxybutyric acid, (1:1-dimethyl-2:3-diphenylbutyrolactone), and had been formed by the reduction of *α-desylisobutyric acid*, the primary product of the reaction. (See also the synthesis of this lactone described later on.)

Analysis gave figures agreeing with the foregoing formula.

0.1656 gave 0.4924 CO₂ and 0.1013 H₂O. C = 81.09 ; H = 6.79.

0.1668 „ 0.4962 CO₂ „ 0.1033 H₂O. C = 81.13 ; H = 6.88.

C₁₈H₁₈O₂ requires C = 81.20 ; H = 6.76 per cent.

In another experiment the alcoholic mother liquor from the foregoing compound deposited eight-sided rectangular laminae of a neutral substance melting at 145—150°, which we were unable to identify.

Half a gram of this dimethyldiphenylbutyrolactone was warmed on the water-bath with an excess of 5 per cent. alcoholic potassium hydroxide. The mixture set to a thick paste. The substance which remained after expelling the alcohol dissolved without residue in cold water; but, on warming the solution, a crystalline powder separated. After recrystallisation from alcohol, it formed flat prisms melting at 106°. It was identified as *dimethyldiphenylbutyrolactone* by the mixture melting-point test.

The lactone had therefore formed, with alcoholic potash, a soluble salt of *aa-dimethyl-βγ-diphenyl-γ-hydroxybutyric acid*,

but on warming the aqueous solution, the salt had been hydrolysed and the resulting acid re-lactonised.

Reduction of α-Desylisobutyric Acid with Sodium in boiling Alcohol: Formation of Dimethyldiphenylbutyrolactone.—The constitution of the foregoing lactone can be proved by preparing it from *α-desylisobutyric acid* by reduction.

1·3 grams of *α-desylisobutyric acid* were reduced in boiling alcoholic solution with 2·6 grams of sodium. The product was diluted with water, acidified with dilute sulphuric acid, and extracted with ether. Sodium carbonate removed from the ether a small quantity of an acid which crystallised from alcohol in slender needles melting at 142°. (Not identified.) The neutral substance remaining after evaporation of the ether crystallised from ether in the flat prisms of *dimethyldiphenylbutyrolactone* melting at 106°. It was further identified by the mixture melting-point test.

Reduction of Dimethyldiphenylbutyrolactone with Hydriodic Acid: Formation of aa-Dimethyl-βγ-diphenylbutyric Acid,

—Seven grams of dimethyldiphenylbutyrolactone (m. p. 106°), 60 grams of hydriodic acid (sp. gr. 1·7), and 2 grams of red phosphorus were heated in a sealed tube at 150° for 5 hours. The product was purified in the ordinary way. An organic acid (yield 0·6 gram), crystallising from alcohol in short prisms melting at 172°, was obtained, whilst 5·4 grams of unchanged substance were recovered.

In the second experiment the mixture was heated to 160—180°. A quarter of the substance was converted into the acid melting at 172°; but the remainder of the product was a thick neutral oil. It is therefore more advantageous to conduct the reduction at 150°.

The acid melting at 172° gave figures agreeing with the formula of *aa*-dimethyl- $\beta\gamma$ -diphenylbutyric acid.

0.1654 gave 0.4873 CO_2 and 0.1118 H_2O . $\text{C} = 80.35$; $\text{H} = 7.51$.

0.1632 „ 0.4811 CO_2 „ 0.1102 H_2O . $\text{C} = 80.39$; $\text{H} = 7.50$.

$\text{C}_{18}\text{H}_{20}\text{O}_2$ requires $\text{C} = 80.59$; $\text{H} = 7.46$ per cent.

The silver salt was obtained as a white precipitate by adding silver nitrate to a solution of the ammonium salt. The value for silver was found somewhat low.

0.3929 gave 0.1104 Ag. $\text{Ag} = 28.09$.

$\text{C}_{18}\text{H}_{19}\text{O}_2\text{Ag}$ requires $\text{Ag} = 28.78$.

Oxidation of aa-Dimethyl- $\beta\gamma$ -diphenyl- γ -hydroxybutyric Acid to α -Desylisobutyric Acid.—Two grams of dimethyldiphenylbutyrolactone were treated with excess of alcoholic potassium hydroxide and the mixture evaporated to dryness on the water-bath. The residue was dissolved in cold water, and a solution of potassium permanganate was added until the coloration was permanent. The liquid was filtered from the hydrated manganese oxides, acidified, and extracted with ether. Dilute sodium carbonate removed from the ethereal solution 0.4 gram of an acid which crystallised from alcohol in flat needles melting, with decomposition, at 218° . These are the properties of *α -desylisobutyric acid*. The substance was further identified by the mixture melting-point test. A considerable proportion (1.3 gram) of dimethyldiphenylbutyrolactone was recovered unchanged.

On analysis the acid gave figures agreeing with those required for *α -desylisobutyric acid*.

0.1582 gave 0.4430 CO_2 and 0.0917 H_2O . $\text{C} = 76.37$; $\text{H} = 6.44$.

$\text{C}_{18}\text{H}_{18}\text{O}_3$ requires $\text{C} = 76.59$; $\text{H} = 6.38$ per cent.

The foregoing three papers form a continuation of a general investigation of the reactions of ketonic compounds (compare *Trans.*, 1897, 71, 123), and the expenses incidental to the work have for many years past been in great part defrayed by repeated allotments from the Government Grant of the Royal Society.

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