CCXXX.—*Isomerides of Anhydroacetonebenzil and its Derivatives.*

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By treating the acetyl derivatives of benzylideneanhydroacetonebenzil and $\beta\beta$ -dimethylanhydroacetonebenzil (see preceding paper) with alcoholic potash, substances were obtained isomeric with the parent compounds, but differing from these in physical and chemical behaviour. The products of deacetylation are soluble in aqueous potassium hydroxide, and are precipitated from the solution with carbon dioxide, thus behaving like monohydric phenols; they also give the ferric chloride colour test characteristic of these compounds.

Japp and Knox treated the acetyl derivative of β -isopropylideneanhydroacetonebenzil in the same way with alcoholic potash. The resulting substance was not isolated in the pure state, but it showed no sign of dissolving in aqueous potassium hydroxide, and I found that it did not give a coloration with ferric chloride, so that the deacetylation in this case does not seem to proceed in the same way as do the deacetylations already mentioned.

In the two cases mentioned above, where deacetylation leads to new phenolic compounds, the constitution of the latter has been investigated, and it has been found that benzylideneanhydroacetonebenzil (3 : 4-diphenyl-5-benzylidene- Δ^2 -cyclopenten-1-one-4-ol) yields 3 : 4-diphenyl-5-benzylidene- Δ^2 -cyclopenten-1-one-2-ol,

and $\beta\beta$ -dimethylanhydroacetonebenzil (3 : 4-diphenyl-5 : 5-dimethyl- Δ^2 -cyclopenten-1-one-4-ol) gives 3 : 4-diphenyl-5 : 5-dimethyl- Δ^2 -cyclopenten-1-one-2-ol,

On deacetylation of their acetyl derivatives (prepared by means of acetic anhydride and sulphuric acid), the 2-hydroxy-compounds are regenerated.

When the results obtained with boiling acetic anhydride alone as an acetylating agent are considered, there are introduced in the case of the first substance, possibilities which make the changes more complicated than the above. This will be explained later.

Thus, in the present research, 2-hydroxy-compounds have been obtained isomeric with two of the eight 4-hydroxy-compounds mentioned in the list given at the beginning of the preceding paper. In the case of one of the three 4-hydroxy-compounds which give acetyl derivatives, hydrolysis does not yield a 2-hydroxy-isomeride, so that in the case of the five substances from which acetyl derivatives have not been prepared, the method of the present research might not lead to 2-hydroxy-isomerides even if acetyl derivatives or other esters should be prepared, and even if the 2-position in the five-carbon ring is occupied by the hydrogen atom. But other methods may be available. In fact, the 2-hydroxy-isomeride of anhydroacetonebenzil itself has been prepared by Vorländer and Schroedter (*Ber.*, 1903, **36**, 1490; compare also Vorländer and von Liebig, *Ber.*, 1904, **37**, 1133; von Liebig, *Diss.*, Halle, 1904; and Metge, *Diss.*, Halle, 1904).

Vorländer and Schroedter, by acting with acetic anhydride and a large quantity of concentrated sulphuric acid on dibenzylideneacetone, obtained a substance, $C_{17}H_{13}O_2Ac(H \cdot SO_3H)$, from which, on hydrolysis, was obtained a compound, $C_{17}H_{14}O_2$, to which they assigned the constitution:

The constitution of the intermediate compound, $C_{17}H_{13}O_2Ac(H \cdot SO_3H)$ has not been ascertained, but the fact that the final reduction product of the 2-hydroxy-compound (namely, the hydrocarbon, $C_{17}H_{18}$ or $\begin{array}{c} CHPh \cdot CH_2 \\ | \\ CHPh \cdot CH_2 \end{array} > CH_2$) is obtained from the sulphurous acid compound, from the 2-hydroxy-compound, and from the intermediate reduction product of the 2-hydroxy-compound (namely, from the ketone, $C_{17}H_{16}O$, $\begin{array}{c} CHPh \cdot CH_2 \\ | \\ CHPh - CO \end{array} > CH_2$, or $\begin{array}{c} CHPh \cdot CH_2 \\ | \\ CHPh \cdot CH_2 \end{array} > CO$) by reduction with hydriodic acid, is given as evidence in support of the theory that the five-carbon ring is present in the intermediate compound,

and against the theory that the closing of the five-carbon ring takes place on hydrolysis. It cannot be maintained, however, that the position in the ring occupied by the acetoxy-group is the same as that occupied by the hydroxyl group of the 2-hydroxy-compound obtained on hydrolysis. Further, in the light of the results here described, it seems possible that the first hydroxyl group may occupy the 4-position. Thus, the method of preparing the acetyl derivative of the 2-hydroxy-compound, and then treating it with sodium hydrogen sulphite, the method adopted by Metge in attempting unsuccessfully to synthesise the compound, $C_{17}H_{13}O_2Ac(H \cdot SO_3H)$, even

if it gave a substance of the desired percentage composition, might lead to one of different constitution.

In defence of the constitution given above for the substance $C_{17}H_{14}O_2$, Vorländer quotes the following experimental results :

Boiling with concentrated aqueous potassium hydroxide gave deoxybenzoin and monomethylstilbene, $C_6H_5 \cdot CMe : CH \cdot C_6H_5$, showing that the following change had occurred :

the two β -carbon atoms of dibenzylideneacetone uniting, and the five-carbon ring being formed.

Oxidation with chromic acid or with permanganate gave benzil and desylacetic acid, $CHPhBz \cdot CH_2 \cdot CO_2H$.

This, [and the fact that a benzylidene derivative was formed by condensation with benzaldehyde, agree with the structure :

As far as these results are concerned, the constitution might be

No sign of a quinoxaline derivative has been observed on treatment with *o*-phenylenediamine, so that the former formula is improbable. The latter is therefore chosen ; and this is confirmed by the acid properties of the substance, and the formation of acetyl and benzoyl derivatives.

The benzylidene derivative of Vorländer's 2-hydroxy-compound, referred to above, is of considerable importance in connexion with the present research. Before knowing that von Liebig had prepared this derivative, it occurred to the author that it might be of interest to prepare this substance from Vorländer's 2-hydroxy-compound and to compare it with the 2-hydroxy-isomeride of benzylideneanhydroacetonebenzil, obtained by the method described in the present paper. It was to be expected that these two benzylidene compounds would be identical.

The benzylidene-2-hydroxy-compound prepared, for comparison, by Vorländer's method had the correct percentage composition, $C_{24}H_{18}O_2$, and agreed with the description given by von Liebig, crystallising in fine, yellow needles (m. p. 223°).

The benzylidene-2-hydroxy-compound obtained from benzylideneanhydroacetonebenzil had the same appearance, but melted at 216° .

These two compounds are chemical isomerides. This is not a case of dimorphism, but, perhaps, of maleoid and fumaroid isomerism.

The two substances give the same dark brown coloration with ferric chloride, and they yield, on acetylation in the cold with acetic anhydride and sulphuric acid, the same acetyl derivative (yellow needles, m. p. 175—176°), from which, on deacetylation, the 2-hydroxy-compound, melting at 216°, is obtained. It should be noted, however, that in this acetylation of the 2-hydroxy-compound melting at 216°, a very small quantity of another substance (acetyl derivative) is obtained, crystallising in almost colourless plates, melting at 148—152° (softening at 148°).

Again, these 2-hydroxy-compounds, when boiled with acetic anhydride alone, both give the same acetyl derivative, crystallising in almost colourless plates, melting at 148—152° (according to von Liebig, almost colourless, oblique prisms, m. p. 148—149°), which was shown by the mixed melting-point test to be the same as the substance obtained in small quantity by acetylation with acetic anhydride and sulphuric acid. The acetyl derivative melting at 148—152° yields, on deacetylation, the 2-hydroxy-compound melting at 223°.

The direct transformation of the more soluble and less stable 2-hydroxy-compound, melting at 216°, into the less soluble and more stable 2-hydroxy-compound, melting at 223°, can be effected by means of a concentrated solution of hydrogen chloride in absolute alcohol. The 2-hydroxy-compounds may have the configurations :

No experimental results, however, are available for settling which of these configurations is to be assigned to the more stable substance, nor are there even, so far as the author is aware, any analogies which might serve as a guide in arriving at a conclusion.

Experiments carried out with the 2-hydroxy-isomeride of $\beta\beta$ -dimethylanhydroacetonebenzil, $\text{C}_{19}\text{H}_{18}\text{O}_2$ (m. p. 155—156°), lead to a constitution similar to that given by Vorländer to the 2-hydroxy-isomeride of anhydroacetonebenzil :

(1) Oximation experiments were successful in the case of $\beta\beta$ -dimethylanhydroacetonebenzil and its acetyl derivative, but failed in the case of the 2-hydroxy-compound, with which hydroxylamine seems to react, giving two substances, of which the amounts obtained were too small for analysis. A phenylhydrazone, however, is obtained with the 2-hydroxy-compound. These results show the presence of one carbonyl group in each of the substances examined.

(2) A methyl ether, $\text{C}_{19}\text{H}_{17}\text{O}(\text{OMe})$ (m. p. 88·5°), and an acetyl derivative, $\text{C}_{19}\text{H}_{17}\text{O}(\text{OAc})$ (m. p. 92·5°), were obtained.

(3) Reduction of the 2-hydroxy-compound with hydriodic acid

yields a neutral substance, $C_{19}H_{20}O$ (m. p. 153°), which reacts with hydroxylamine; to this substance the formula

may be assigned.

$\beta\beta$ -Dimethylanhydroacetonebenzil should, on reduction, yield the same product, but no definite substance could be isolated from this reaction.

(4) Oxidation with permanganate or with hydrogen peroxide gives α -desylisobutyric acid, $COPh \cdot CHPh \cdot CMe_2 \cdot CO_2H$.

(5) Oxidation with potassium hypobromite gives an acid, $C_{19}H_{20}O_5$ (m. p. 197°), to which the following constitution has been assigned:

This structure agrees with the following properties of this acid: (a) It loses a molecule of water at 113° . (b) It is inert towards acetylating agents. (c) It is inert towards hydriodic acid unless the mixture is heated with red phosphorus in a sealed tube at 150° , when it yields $\beta\gamma$ -diphenyl- $\alpha\alpha$ -dimethylbutyric acid, $CH_2Ph \cdot CHPh \cdot CMe_2 \cdot CO_2H$, and the lactone of γ -hydroxy- $\beta\gamma$ -diphenyl- $\alpha\alpha$ -dimethylbutyric acid,

(d) It is a monobasic acid, as shown by the analysis of its silver salt and by titration with standard alkali.

(e) It is a lactone of the acid $CO_2H \cdot CPh(OH) \cdot CHPh \cdot CMe_2 \cdot CO_2H$, the disodium salt of which has been prepared from the acid $C_{19}H_{20}O_5$, the lactone ring being broken in the process.

(6) The experiments with potassium hydroxide were of considerable importance in the case of Vorländer's 2-hydroxy-compound, showing, as they did, that the two β -carbon atoms of dibenzylideneacetone had united, the five-carbon ring being formed. Now, although the same experiment does not throw the same light on the constitution of the 2-hydroxy-isomeride of $\beta\beta$ -dimethylanhydroacetonebenzil (the benzil residue being already present in $\beta\beta$ -dimethylanhydroacetonebenzil), it seemed likely that the product obtained would be *isopropylstilbene* on the analogy of Vorländer's experiment which gives monomethylstilbene, thus:

The product, however, was stilbene itself. This result is not to be

regarded as inconsistent with the constitution indicated by the other experiments described in this paper.

The oxidation experiments and the empirical formula show that the structure of the 2-hydroxy-compound must be

Acetylation and methylation experiments show that the substance contains a hydroxyl group, and the action of phenylhydrazine proves the presence of a carbonyl group; consequently, the only way of accounting for these is by the expression

This formula is consistent, not only with the chemical properties of the substance itself, but also with the results obtained by Vorländer in his experiments on the 2-hydroxy-isomeride of anhydroacetonebenzil.

EXPERIMENTAL.

Benzylideneanhydroacetonebenzil.

On repeating Japp and Findlay's method of preparation of this substance (Trans., 1899, 75, 1023), there was found in the first hot alcoholic extract of the crude product (which Japp and Findlay assumed to give unchanged anhydroacetonebenzil) a substance crystallising in prisms, melting at 213.5°. Subsequent extracts yielded six-sided plates (m. p. 232°).

The substance melting at 213.5° was found to be isomeric with benzylideneanhydroacetonebenzil:

0.1472 gave 0.4582 CO₂ and 0.0740 H₂O. C = 84.96; H = 5.59.

C₂₄H₁₈O₂ requires C = 85.20; H = 5.32 per cent.

The substance melting at 232° had the appearance and melting point hitherto assigned to benzylideneanhydroacetonebenzil.

When treated with acetic anhydride and concentrated sulphuric acid, these two substances give the same acetyl derivative, melting at 175° (see preceding paper). They are different forms of benzylideneanhydroacetonebenzil, perhaps maleoid and fumaroid isomerides.

Japp and Findlay found (Trans., 1899, 75, 1018) that acetic anhydride alone did not act on benzylideneanhydroacetonebenzil (m. p. 232°) even when the temperature was raised to 150°; this is of

* The substance is not only an enol, but also a ketone *at the same time*, and Vorländer uses the term "keto-enol" in referring to a compound of this kind. This name has, however, been rejected by the present author, because in what is usually called "keto-enolic isomerism" the substance is an enol and a ketone *alternately*.

interest in connexion with the behaviour of the two 2-hydroxy-isomerides.

The yield of the substance melting at 213.5° was small, whilst about 24 grams of the substance melting at 232° were obtained from 20 grams of anhydroacetonebenzil.

An attempt to transform from the one substance to the other was not successful. There are indications, however, that the substance melting at 213.5° can be converted into the substance melting at 232° by means of an alcoholic solution of hydrogen chloride.

3 : 4-Diphenyl-5-benzylidene- Δ^2 -cyclopenten-1-one-2-ol (m. p. 216°),

Eight grams of the acetyl derivative (m. p. 175°) of benzylidene-anhydroacetonebenzil were mixed with an excess of a 5 per cent. alcoholic solution of potassium hydroxide. The acetyl derivative dissolved, giving a red solution, and much heat was developed. This solution was kept at the ordinary temperature for a few days. If water is added to the red liquid, a brilliant red solid is obtained, but if the red liquid is acidified with hydrochloric acid, the red colour disappears and a yellow precipitate is formed. This dissolves in aqueous potassium hydroxide, from which it is reprecipitated by carbon dioxide. Its alcoholic solution gives with a drop of ferric chloride solution a dark brown coloration.

The substance crystallises from alcohol in small clusters of fine needles melting at 216° :

0.1646 gave 0.5157 CO_2 and 0.0794 H_2O . C = 85.45; H = 5.36.

$\text{C}_{24}\text{H}_{18}\text{O}_2$ requires C = 85.20; H = 5.32 per cent.

3 : 4-Diphenyl-5-benzylidene- Δ^2 -cyclopenten-1-one-2-ol (m. p. 223°).

3 : 4-Diphenyl- Δ^2 -cyclopenten-1-one-2-ol was prepared by the method described by Vorländer (*loc. cit.*); the following points require special attention.

During the gradual addition of sulphuric acid, the temperature should not be allowed to fall lower than $25\text{--}30^{\circ}$, the temperature recommended by Vorländer.

After the addition of all the acid, too long a time should not elapse before the mixture is worked up. The whole preparation should be carried out in one day. Further, in heating with alkali to effect hydrolysis of the intermediate sulphurous acid compound, sufficient time should be given for the reaction to be completed, otherwise, on acidifying, there will be obtained a product difficult to purify.

One gram of 3 : 4-diphenyl- Δ^2 -cyclopenten-1-one-2-ol was dissolved in 30 c.c. of absolute alcohol containing 1 gram of potassium hydroxide, and 0.5 gram of benzaldehyde was added. This mixture was kept at the ordinary temperature for four days. On adding it to a large bulk of water, a clear solution was obtained, and, on passing carbon dioxide through it, an orange-coloured precipitate was obtained, which crystallised from hot alcohol in clusters of light yellow needles melting at 220°. Von Liebig gives the melting point 223—224°, and by employing another method of preparing this substance, the present author obtained it with the melting point 223°. The product is therefore probably identical with von Liebig's compound, although the melting points differ slightly. The yield of pure substance recrystallised from alcohol was 0.55 gram :

0.1464 gave 0.4560 CO₂ and 0.07 H₂O. C = 84.94 ; H = 5.31.

C₂₄H₁₈O₂ requires C = 85.20 ; H = 5.32 per cent.

This substance is also obtained when the 2-hydroxy-compound melting at 216° is added to enough of a concentrated solution of hydrogen chloride in absolute alcohol to give a clear solution ; it crystallises from this solution in a very pure state, and in large amount.

2-Acetoxy-3 : 4-diphenyl-5-benzylidene- Δ^2 -cyclopentenone

When the 2-hydroxy-compound melting at 216° was treated with acetic anhydride and a few drops of sulphuric acid at the ordinary temperature, two products were obtained, the chief of which crystallised from alcohol in very fine needles melting at 175—176°, and retaining their form on recrystallisation. From the alcoholic mother liquor there separated a very small quantity of almost colourless, rhombic plates, the melting point of which was rather indefinite. The substance softened at about 148—149°, and melted to a clear liquid a few degrees higher.

Analysis of the compound melting at 175—176° :

0.0936 gave 0.2795 CO₂ and 0.0468 H₂O. C = 81.43 ; H = 5.55.

C₂₆H₂₀O₃ requires C = 82.10 ; H = 5.26 per cent.

A mixture of the acetyl derivative (m. p. 175°) of benzylidene-anhydroacetonebenzil and the acetyl derivative (m. p. 175—176°) of the 2-hydroxy-compound melted at 155°, showing that these substances, although they have the same composition and melting point, are not identical.

This substance (m. p. 175—176°) may also be prepared by the action

of acetic anhydride and sulphuric acid at the ordinary temperature on the 2-hydroxy-compound melting at 223°.

The hydrolysis of this ester may be effected by means of 5 per cent. alcoholic potash, the method being similar to that employed in the preparation of 3:4-diphenyl-5-benzylidene- Δ^2 -cyclopenten-1-one-2-ol (p. 2144); the 2-hydroxy-compound melting at 216° is obtained.

2-Acetoxy-3:4-diphenyl-5-benzylidene- Δ^2 -cyclopentenone
(m. p. 148—152°).

A mixture of 12 grams of acetic anhydride and 0.6 gram of the 2-hydroxy-compound melting at 216° was boiled for one and a-half hours. The product obtained on adding water crystallised from benzene in almost colourless, rhombic plates, which soften at 148—149° and melt to a clear liquid at about 152°. Liebig, by the action of boiling acetic anhydride on the 2-hydroxy-compound melting at 223°, obtained an acetyl derivative which he describes as consisting of almost colourless, oblique prisms melting at 148—149°. These acetyl derivatives are doubtless the same.

On hydrolysis by means of 5 per cent. alcoholic potash, the 2-hydroxy-compound melting at 223° is obtained.

From the hydrolysis experiments, therefore, the acetyl derivative melting at 148—152° corresponds with the 2-hydroxy-compound melting at 223°, and the acetyl derivative melting at 175—176° corresponds with the 2-hydroxy-compound melting at 216°.

3:4-Diphenyl-5:5-dimethyl- Δ^2 -cyclopenten-1-one-2-ol,

Five grams of the acetyl derivative (m. p. 137°) of $\beta\beta$ -dimethyl-anhydroacetonebenzil were added to 50 c.c. of a 5 per cent. alcoholic solution of potassium hydroxide. Where the alkali came in contact with the solid acetyl compound, a bright green colour was observed, which disappeared on shaking. A yellow solution was obtained, which was kept at the ordinary temperature for several days. On acidification, the 2-hydroxy-compound was precipitated, which crystallised from alcohol, in which it is very soluble, in pink needles melting at 155—156°. The yield was 4.2 grams:

0.1481 gave 0.4436 CO₂ and 0.0868 H₂O. C = 81.68; H = 6.51.

C₁₉H₁₈O₂ requires C = 82.01; H = 6.47 per cent.

This substance dissolves in aqueous potassium hydroxide, from which it is reprecipitated by carbon dioxide. Its alcoholic solution gives with ferric chloride solution a dark brown coloration.

The *phenylhydrazone* crystallises from benzene in very small, yellow plates, melting and decomposing at 244° :

0.1820 gave 0.5466 CO_2 and 0.1152 H_2O . $\text{C} = 81.91$; $\text{H} = 7.03$.

$\text{C}_{25}\text{H}_{24}\text{ON}_2$ requires $\text{C} = 81.52$; $\text{H} = 6.52$ per cent.

The *oxime* of the isomeric 4-hydroxy-compound ($\beta\beta$ -dimethyl-anhydroacetonebenzil) crystallises from alcohol in large, prismatic plates, melting and decomposing at 190° :

0.2554 gave 10.5 c.c. N_2 (moist) at 17° and 761.5 mm. $\text{N} = 4.77$.

$\text{C}_{19}\text{H}_{19}\text{O}_2\text{N}$ requires $\text{N} = 4.77$ per cent.

The *oxime* of 4-acetoxy-3:4-diphenyl-5:5-dimethyl- Δ^2 -cyclopentenone crystallises from alcohol in fine, satiny, white needles, melting and decomposing at 164° :

0.2746 gave 10 c.c. N_2 (moist) at 19° and 772.7 mm. $\text{N} = 4.26$.

$\text{C}_{21}\text{H}_{21}\text{O}_3\text{N}$ requires $\text{N} = 4.17$ per cent.

On methylation of the 2-hydroxy-compound melting at 155 — 156° with methyl iodide in the presence of sodium methoxide by Japp and Klingemann's modification of the method (Trans., 1888, 53, 526), 2-methoxy-3:4-diphenyl-5:5-dimethyl- Δ^2 -cyclopentenone was obtained; this crystallises from alcohol in short needles, melting at 88.5° :

0.1430 gave 0.4308 CO_2 and 0.0890 H_2O . $\text{C} = 82.17$; $\text{H} = 6.92$.

$\text{C}_{20}\text{H}_{20}\text{O}_2$ requires $\text{C} = 82.19$; $\text{H} = 6.85$ per cent.

Boiling with ethyl alcohol and sulphuric acid did not effect etherification.

On acetylation of the 2-hydroxy-compound melting at 155 — 156° with acetic anhydride and sulphuric acid at the ordinary temperature in the usual way, there was obtained 2-acetoxy-3:4-diphenyl-5:5-dimethyl- Δ^2 -cyclopentenone, which crystallises from alcohol in very slender needles, and from light petroleum in large, six-sided plates melting at 92.5° :

0.1486 gave 0.4290 CO_2 and 0.0866 H_2O . $\text{C} = 78.72$; $\text{H} = 6.47$.

$\text{C}_{21}\text{H}_{20}\text{O}_3$ requires $\text{C} = 78.75$; $\text{H} = 6.25$ per cent.

Hydrolysis of this ester by means of 5 per cent. alcoholic potash regenerates the 2-hydroxy-compound melting at 155 — 156° .

3:4-Diphenyl-5:5-dimethylcyclopentanone,

A mixture of 10 grams of diphenyldimethyl- Δ^2 -cyclopentenon-2-ol (m. p. 155 — 156°), 15 grams of hydriodic acid (D 1.7), and 20 grams of red phosphorus was heated to boiling for two hours. The product crystallised from alcohol in large, prismatic plates, melting at 153° . The yield was about 5 grams.

Boiling for five minutes with concentrated hydriodic acid (D 1.96) gives a small quantity of the same product, but most of the 2-hydroxy-compound remains unchanged:

0.1462 gave 0.4626 CO_2 and 0.1014 H_2O . C = 86.28; H = 7.70.

$\text{C}_{19}\text{H}_{20}\text{O}$ requires C = 86.36; H = 7.57 per cent.

The *oxime* crystallises from alcohol as $4\text{C}_{19}\text{H}_{21}\text{ON}, \text{EtOH}$. The alcohol of crystallisation is removed at 110° :

0.3620 gave 16.2 c.c. N_2 (moist) at 13° and 769 mm. N = 5.35.

$\text{C}_{19}\text{H}_{21}\text{ON}$ requires N = 5.0 per cent.

α -Desylisobutyric acid, $\text{COPh}\cdot\text{CHPh}\cdot\text{CMe}_2\cdot\text{CO}_2\text{H}$.

Nine grams of the 2-hydroxy-compound melting at $155\text{--}156^\circ$ were mixed with 18 grams of potassium permanganate and aqueous potassium hydroxide, and kept at the ordinary temperature. The clear filtrate, on being acidified with hydrochloric acid, gave a precipitate, which was dissolved in ether, and the ethereal solution was shaken with sodium carbonate solution. The sodium carbonate extract gave an acid, which was recrystallised from alcohol, and melted, when rapidly heated, at 218° , with evolution of gas:

0.1521 gave 0.4268 CO_2 and 0.0880 H_2O . C = 76.52; H = 6.43.

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

Japp and Michie (Trans., 1903, 83, 309) synthesised *α -desylisobutyric acid* (m. p. 218°), and a mixed melting-point test showed the two acids to be identical.

On treating this acid with acetic anhydride and sulphuric acid at the ordinary temperature, *$\beta\gamma$ -diphenyl- $\alpha\alpha$ -dimethyl- Δ^2 -crotonolactone* (m. p. $105\text{--}106^\circ$) was obtained, this being further proof of the identity of the substance (Japp and Michie, *loc. cit.*).

α -Desylisobutyric acid was also obtained by oxidising an alkaline solution of the 2-hydroxy-compound melting at $155\text{--}156^\circ$ with hydrogen peroxide. The product of this oxidation on melting yielded a substance melting at 106° , and the author also found that *α -desylisobutyric acid* decomposed in the same way.

$\beta\gamma$ -Diphenyl- $\alpha\alpha$ -dimethylbutyrolactone- γ -carboxylic Acid,

Ten grams of the 2-hydroxy-compound melting at $155\text{--}156^\circ$ were dissolved in a solution of 60 grams of potassium hydroxide in 600 c.c. of water. To this solution was added an alkaline solution of potassium hypobromite, prepared by adding 30 grams of bromine to a solution of 60 grams of potassium hydroxide in 600 c.c. of water. The cold

mixture was kept for two days. A slight precipitate which had formed was then removed, and sulphur dioxide was passed into the cold filtrate. A precipitate was obtained, and the precipitation was completed by acidifying with dilute sulphuric acid. The solid was dissolved in ether, and the ethereal solution was treated with successive portions of an aqueous solution of sodium carbonate and then of an aqueous solution of sodium hydroxide. Practically nothing was obtained in the sodium hydroxide extract. The sodium carbonate yielded an acid which was difficult to purify by recrystallisation from the usual solvents. The method finally adopted was to prepare the pure potassium salt and to acidify its aqueous solution. The acid, further purified by recrystallisation from dilute alcohol, separated in needles melting at 197° .

It is very soluble in alcohol, acetic acid, or benzene, and insoluble in light petroleum. The yield was about 5 grams.

When sodium hypochlorite was used instead of potassium hypobromite, the yield was not improved. Other experiments, in which the proportion of bromine was increased and the temperature raised to that of the water-bath, led to similar results :

0.2014 gave 0.5118 CO_2 and 0.1093 H_2O . $\text{C} = 69.3$; $\text{H} = 6.0$.

$\text{C}_{19}\text{H}_{20}\text{O}_5$ requires $\text{C} = 69.5$; $\text{H} = 6.0$ per cent.

The acid crystallises with one molecule of water of crystallisation :

0.3510 lost 0.0190 at 113° . $\text{H}_2\text{O} = 5.4$.

$\text{C}_{19}\text{H}_{18}\text{O}_4 \cdot \text{H}_2\text{O}$ requires $\text{H}_2\text{O} = 5.5$ per cent.

The crystals effloresce appreciably even under ordinary conditions of temperature and pressure, so that, unless the specimen analysed has been quite recently prepared, the content of water is found too low.

The *silver* salt was prepared :

0.2326 gave 0.0566 Ag. $\text{Ag} = 24.33$.

$\text{C}_{19}\text{H}_{19}\text{O}_5\text{Ag}$ requires $\text{Ag} = 24.82$ per cent.

0.4534 of the acid required 7.22 c.c. of alcoholic sodium ethoxide (1 c.c. = 0.00446 gram Na). M.W. (for a monobasic acid) = 324.5.

$\text{C}_{19}\text{H}_{20}\text{O}_5$ requires M.W. = 328.

The acid is shown below to be a lactone of α -hydroxy- $\alpha\beta$ -diphenyl- $\gamma\gamma$ -dimethylglutaric acid, $\text{CO}_2\text{H} \cdot \text{CPh}(\text{OH}) \cdot \text{CHPh} \cdot \text{CMe}_2 \cdot \text{CO}_2\text{H}$. The formation of a little of the sodium salt of this dibasic acid before the neutral point is reached may explain the excess of alkali required in the above titration.

The acid is inert towards acetic anhydride containing a few drops of concentrated sulphuric acid, and towards boiling acetic anhydride.

On reduction with hydriodic acid and red phosphorus by heating for

three hours at 150° in a sealed tube, the acid gave $\beta\gamma$ -diphenyl- $\alpha\alpha$ -dimethylbutyric acid, which was obtained by Japp and Michie (Trans., 1903, 83, 311, 312), and also $\beta\gamma$ -diphenyl- $\alpha\alpha$ -dimethylbutyrolactone. Both these products were identified by the mixed melting-point test.

$\beta\gamma$ -Diphenyl- $\alpha\alpha$ -dimethylbutyrolactone- γ -carboxylic acid was dissolved in absolute alcohol, and a solution of sodium ethoxide in absolute alcohol was added in excess of that required for the formation of a dibasic salt. Phenolphthalein indicated the point at which enough sodium ethoxide was added to form the monobasic salt. When excess of twice this quantity of sodium ethoxide solution had been run in, and the solution had been gently heated, a bulky precipitate of the dibasic salt was obtained. The pure white sodium salt was collected and washed with absolute alcohol.

The salt crystallises with two molecules of alcohol of crystallisation, which are partly lost in a vacuum over sulphuric acid, and completely at 110° :

0.5820 gave 0.2218 Na_2SO_4 . Na = 12.36.

$\text{C}_{19}\text{H}_{18}\text{O}_5\text{Na}_2$ requires Na = 12.39 per cent.

Enough water must have been present in the "absolute" alcohol for the reaction to take place, as the dibasic salt is formed even if the acid melting at 197° is free from water of crystallisation before use in this experiment.

Action of Potassium Hydroxide on 3:4-Diphenyl-5:5-dimethyl- Δ^2 -cyclopenten-1-one-2-ol.

Stilbene, identified by analysis, by the mixed melting-point test, and by the preparation and analysis of the dibromo-derivative, was obtained by boiling the 2-hydroxy-compound melting at 155 – 156° with 50 per cent. aqueous potassium hydroxide. A small quantity of a substance melting at 157° was also obtained.

The experiment was repeated with various percentages of the alkali; with all the concentrations used (from 15 per cent. upwards), a little of the substance melting at 157° was isolated; with the lower concentrations, the main bulk of the 2-hydroxy-compound was unchanged, and no stilbene was formed; with the higher concentrations, stilbene was obtained, and the yield improved as the alkali concentration increased.

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