CVII.—*Reduction of $\alpha\gamma$ -Dibenzoylpropane and Dibenzoyldiphenylbutadiene.*

By FRANCIS R. JAPP, F.R.S., and ARTHUR C. MICHIE, B.Sc.

JOHANNES WISLICENUS has published, conjointly with some of his pupils (*Annalen*, 1898, 302, 191—244), a series of papers under the collective title, "Formation of Carbocyclic Compounds by the Conversion of 1:5- and 1:6-Diketones into their Pinacones." Portions of the investigation treat of matters which have already been dealt with by other methods in papers on the condensations of benzil with ketones published by one of us in conjunction with various collaborators; but of the latter work, unfortunately everything except the first paper—"On Additive and Condensation Compounds of Diketones with Ketones" (Japp and Miller, *Trans.*, 1885, 47, 11; also *Ber.*, 1885, 18, 179)—has escaped the notice of the German investigators. The consequence is that they occasionally describe, as new, facts already known; that they fail to compare their compounds with others previously described, even where this is of importance and that they sometimes misinterpret their results. We have therefore subjected certain portions of their work to a careful revision.

J. Wislicenus and C. K. Kuhn (*loc. cit.*, p. 215) describe the preparation of $\alpha\gamma$ -dibenzoylpropane; its reduction, by the action of sodium on an ethereal solution of the substance floating on water, to an uncrystallisable oil which they regard as the cyclic pinacone 1:2-diphenyl-1:2-dihydroxycyclopentane, the reaction taking place according to the equation

and, finally, the reduction of the latter compound by hydriodic acid to a substance which they regard as 1:2-diphenylcyclopentane, $\begin{array}{c} \text{C}_6\text{H}_5 \cdot \text{CH} \cdot \text{CH}_2 \\ \text{C}_6\text{H}_5 \cdot \text{CH} \cdot \text{CH}_2 \end{array} > \text{CH}_2$, a white, granular, crystalline mass melting at 108°.

These authors are apparently unaware that a substance claiming to be a 1:2-diphenylcyclopentane (m. p. 47°) has already been prepared. Japp and Burton (*Trans.*, 1887, 51, 423), who obtained it by the reduction of anhydracetonebenzil (*diphenylcyclopentenolone*), $\begin{array}{c} \text{C}_6\text{H}_5 \cdot \text{C} = \text{CH} \\ \text{C}_6\text{H}_5 \cdot \text{C}(\text{CH}) \cdot \text{CH}_2 \end{array} > \text{CO}$, were uncertain whether it was a 1:1-phenylbenzylcyclobutane or a 1:2-diphenylcyclopentane, as the constitution of anhydracetonebenzil itself was not then settled. Japp and Lander

(*Trans.*, 1897, 71, 128 and 131) conclusively showed that it had the latter constitution. Later on, we will briefly recapitulate their arguments, adding a further experimental proof.

Our first impression was that the hydrocarbons melting at 47° and 108° respectively might be the *cis*- (meso) and the *trans*- (racemic) form. We therefore resolved to prepare the hydrocarbon melting at 108° by Wislicenus and Kuhn's method: in the first place, in order to compare the two compounds, and, secondly, to ascertain whether the hydrocarbon melting at 47° was formed at the same time, as, in the method of purification adopted by these authors, it might possibly have been overlooked.

We first prepared $\alpha\gamma$ -dibenzoylpropane and, incidentally, greatly improved the yield of this substance by hydrolysing the dibenzoylglutaric ester with dilute sulphuric acid instead of with caustic alkali. The "acid hydrolysis" of the ketonic ester observed by Wislicenus and Kuhn was thus entirely avoided, and only "ketonic hydrolysis" occurred.

We then reduced the $\alpha\gamma$ -dibenzoylpropane as prescribed by Wislicenus and Kuhn, and obtained the "pale-yellow oil" which they could not induce to crystallise, and which they therefore analysed after leaving it in a vacuum desiccator until the weight was constant. They obtained figures agreeing with those required for the expected cyclic pinacone, 1 : 2-diphenyl-1 : 2-dihydroxycyclopentane.

We find, however, that, by appropriate treatment, no fewer than five distinct substances can be separated from this "pale-yellow oil": (1) the above cyclic pinacone (m. p. 103—104·5°); (2) in small quantity, $\alpha\epsilon$ -diphenyl- $\alpha\epsilon$ -dihydroxypentane,

(m. p. 84—88°), which we were afterwards able to prepare in somewhat larger quantity by reducing $\alpha\gamma$ -dibenzoylpropane with sodium in boiling alcohol; (3) a small quantity of unchanged $\alpha\gamma$ -dibenzoylpropane, which is always present, even when the sodium in Wislicenus and Kuhn's method is used in the enormous excess of more than 20 times the theoretical amount; (4) a colourless oil, soluble in light petroleum, and (5) a yellow resin insoluble in light petroleum. That the "pale-yellow oil" gave, in Wislicenus and Kuhn's hands, figures agreeing with those required for the pinacone, was therefore a pure coincidence.

We found that the pinacone could be obtained much more readily, and in a state of purity, by reducing $\alpha\gamma$ -dibenzoylpropane in hot aqueous alcoholic solution with aluminium amalgam.

Chromium trioxide, in acetic acid solution, readily reconverts the pinacone into $\alpha\gamma$ -dibenzoylpropane.

As regards the hydrocarbon, we prepared it both according to

Wislicenus and Kuhn's directions from the "pale-yellow oil," and afterwards from the pure pinacone. By their method of purification, one and the same substance, agreeing fairly well with their description, was isolated in both cases. It is of very indefinite character and is certainly not a diphenylcyclopentane. Thus it does not boil even at 340° under 12 mm. pressure, whereas 1:2-diphenylcyclopentane from anhydrazetonebenzil boils quite constantly at 189° under 12 mm. pressure. Again, it must appear somewhat strange that Wislicenus and Kuhn's diphenylcyclopentane should melt as high as 108° and be practically insoluble in alcohol, seeing that Wislicenus and Carpenter's tetraphenylcyclopentane (*Annalen*, 1898, 302, 229), in spite of its two additional phenyl groups, melts as low as 81° and is soluble in alcohol.

We have therefore no hesitation in saying that Wislicenus and Kuhn's supposed 1:2-diphenylcyclopentane is a highly polymerised substance, and that the action of hydriodic acid on the pinacone is much less simple than these authors have assumed. Indeed, the known action of acids upon pinacones, in producing dehydration and migration, might have suggested the need for caution on this point.

As it was apparently impossible to obtain 1:2-diphenylcyclopentane from the pinacone, it was of interest to ascertain whether the reverse change could be effected; whether the known 1:2-diphenylcyclopentane (m. p. 47°) from anhydrazetonebenzil could be oxidised either to a pinacone—identical or stereoisomeric with that above described—or, failing this, to $\alpha\gamma$ -dibenzoylpropane. We found that the latter transformation readily takes place when the hydrocarbon is treated with chromium trioxide in acetic acid solution in the cold:

All attempts to obtain an intermediate oxidation product proved fruitless.

The foregoing reaction entirely confirms the constitution of a 1:2-diphenylcyclopentane which Japp and Lander assigned to the hydrocarbon $\text{C}_{17}\text{H}_{18}$ (m. p. 47°) from anhydrazetonebenzil.

Before leaving this part of the subject, we will arrange in their order the different compounds which have been obtained by one of us, conjointly with pupils, in the transformation of benzil and acetone, on the one hand, into $\alpha\gamma$ -dibenzoylpropane, on the other:

The constitution of anhydracetonebenzil has been proved by a study of its reactions, too long to recapitulate here (compare Japp and Lander, *Trans.*, 1897, **71**, 123); that of diphenylcyclopentenone by its formation from anhydracetonebenzil, by its giving a phenylhydrazone, and by its being oxidised quantitatively to diphenylmaleic acid by sodium hypobromite (*ibid.*, 132); and finally, that of 1:2-diphenylcyclopentane both by its formation from diphenylcyclopentenone by reduction, and by its conversion into $\alpha\gamma$ -dibenzoylpropane by oxidation, as also by the fact that it behaves as a saturated compound, both towards bromine and towards hydriodic acid at 150° (*Trans.*, 1887, **51**, 424).*

Wislicenus and Lehmann (*Annalen*, 1898, **302**, 195) have studied the action of alcoholic sodium hydroxide and sodium ethoxide on a mixture of benzil and acetophenone. By the first method they obtained $\alpha\beta$ -dibenzoylphenylethylene ($\alpha\beta$ -dibenzoylcinnamene, anhydracetophenonebenzil),† $\begin{array}{c} \text{C}_6\text{H}_5 \cdot \text{C} : \text{CH} \cdot \text{CO} \cdot \text{C}_6\text{H}_5 \\ \text{C}_6\text{H}_5 \cdot \text{CO} \end{array}$, which they recognised as

identical with the compound obtained by Japp and Miller by the action of warm aqueous potash on a mixture of benzil and acetophenone (*Trans.*, 1885, **47**, 35). Wislicenus and Lehmann's method, however, yields

* It is not often that Dr. M. M. Richter, the author of the invaluable *Lexikon der Kohlenstoff-Verbindungen*, ventures to combine his already sufficiently arduous task of compilation with that of criticism. With regard to the present question, however, after accepting Wislicenus and Kuhn's compound at their own valuation as "1,2-Diphenyl-R-Pentamethylen, Sm. 108," he indicates his scepticism regarding the 1:2-diphenylcyclopentane of m. p. 47° by querying its constitution. Again, Richter-Anschütz's *Organische Chemie* (9th edition, **2**, 10) gives only Wislicenus and Kuhn's compound.

The reasons for this preferential treatment of the non-existent 1:2-diphenylcyclopentane are assuredly not *chemical*.

† I must, I think, decline the responsibility for some, at least, of the changes of name that this compound has undergone. The first systematic name assigned to it by Dr. Klingemann and myself was " $\alpha\beta$ -dibenzoylstyrolene," and under this name it was described in the *Proceedings* (1889, **5**, 136). On our sending the full paper to the *Journal*, Mr. C. E. Groves, at that time Editor, pointed out to us that the official name for "styrolene" was "cinnamene," and that, in any case, the compound would be thus indexed. We therefore made the required change to " $\alpha\beta$ -dibenzoylcinnamene" (compare *Trans.*, 1890, **57**, 662); but I now find that the compound appears in the *Collective Index* as " $\alpha\beta$ -dibenzoylstyrene."—F. R. J.

the compound mixed with dibenzoyldiphenylbutadiene, and is therefore inferior to that described by Japp and Klingemann (Trans., 1890, 57, 673), in which, by employing as a condensing agent alcoholic potassium hydroxide very slightly diluted with water, pure $\alpha\beta$ -dibenzoylphenylethylene is obtained. Wislicenus and Lehmann have overlooked the latter paper, with the result that, in addition to employing the foregoing unsuitable method of preparation, they make various determinations without indicating that these are merely confirmations of some already made: thus an ebullioscopic determination of the molecular weight, already determined cryoscopically by Japp and Klingemann (*ibid.*, 674), and a few indications of the crystalline form (two angles measured), whereas Tutton (Trans., 1890, 57, 714) gives full crystallographical measurements of $\alpha\beta$ -dibenzoylphenylethylene and ten of its derivatives. If this were all, the matter would not, of course, be worth calling attention to. But this want of acquaintance with the foregoing work causes the German authors to go somewhat astray in their interpretation of the chief reaction of their paper—the reduction of dibenzoyldiphenylbutadiene.

Dibenzoyldiphenylbutadiene, which had not been previously prepared, was obtained by Wislicenus and Lehmann (*loc. cit.*, 198) by the condensation of 1 molecular proportion of benzil with 2 of acetophenone under the influence of alcoholic sodium ethoxide. They leave it an open question whether the compound has the symmetrical or the unsymmetrical constitution:

They subjected this compound to the action of various reducing agents, and obtained various products. One of the latter, which was formed by reducing the substance with hydriodic acid in glacial acetic acid solution and boiling the resinous product with alcoholic potassium hydroxide, and to which the formula $\text{C}_{20}\text{H}_{14}\text{O}$ is assigned, attracted our attention; partly because it was difficult to see how it could have such a formula, and partly because it was obviously identical with an already known compound of a different formula. The authors describe the substance as crystallising from alcohol in "long, colourless, flat needles, melting at 92–94°." They found benzoic acid in the alkaline solution from the treatment of the resin, and explain the formation of the compound as follows: "By the action of the alkali, the resinous reduction product of the diketone—the latter a compound containing four phenyl groups—has been broken up into a molecule of benzoic acid and a compound, $\text{C}_{20}\text{H}_{14}\text{O}$, containing three phenyl groups."

Leaving difficulties with the hydrogen out of the question, three phenyl groups would account for C_{18} , leaving C_2 over for the grouping

of these three phenyl groups, and the authors refrain from hazarding any explanation as to how a dibenzoyldiphenylbutadiene, whether symmetrical or unsymmetrical, could yield a compound in which three phenyl groups are attached to the group C_2 .

Speculation on this point is, however, unnecessary, inasmuch as the compound has not the formula $C_{20}H_{14}O$, but $C_{22}H_{16}O$ (Wislicenus and Kuhn's figures agree, on the whole, rather better with this formula than with that which they calculate); and is identical with the substance which Japp and Burton (*Trans.*, 1887, **51**, 430) obtained by the reduction of $\alpha\beta$ -dibenzoylphenylethylene with hydriodic acid. The latter authors describe the compound as forming "colourless, long, flat prisms melting constantly at $92-93^\circ$," which agrees with Wislicenus and Lehmann's description. Japp and Klingemann (*Ber.*, 1888, **21**, 2933; *Trans.*, 1890, **57**, 663) showed later that the compound was 2 : 3 : 5-*triphenylfurfuran*,

We therefore repeated the reduction of dibenzoyldiphenylbutadiene with hydriodic acid, as described by Wislicenus and Lehmann, omitting, however, the boiling with alcoholic potash, and, instead, distilling the product under reduced pressure. We thus obtained without difficulty *acetophenone* and 2 : 3 : 5-*triphenylfurfuran*, the formation of the former of which explains that of the latter. In the first stage of the reaction, the dibenzoyldiphenylbutadiene parts with one $C_6H_5 \cdot CO \cdot CH$ group by hydrolysis as acetophenone, and the resulting $\alpha\beta$ -dibenzoylphenylethylene is then reduced to triphenylfurfuran. Assuming, for simplicity, the symmetrical formula for dibenzoyldiphenylbutadiene, the process may be represented as follows :

The boiling with alcoholic potash employed by Wislicenus and Lehmann, has therefore nothing to do with the formation of the triphenylfurfuran, although this treatment may, of course, have aided in removing impurities.

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The various facts above referred to, which have escaped Wislicenus and Lehmann's notice, are to be found collected together in *Beilstein*, 3, p. 308, in the article "Dibenzoylstyrol."

EXPERIMENTAL.

Preparation of Ethyl Dibenzoylglutarate (Ethyl Methylene dibenzoylacetate), $\text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CH}\cdot\text{CO}\cdot\text{C}_6\text{H}_5$.—This substance was prepared by the condensation of formaldehyde with ethyl benzoylacetate as described by Knoevenagel (*Annalen*, 1894, 281, 57), except that we employed as a condensing agent piperidine instead of diethylamine.* One hundred and twenty grams of ethyl benzoylacetate and 24 grams of a 40 per cent. aqueous solution of formaldehyde were mixed, and 15 grams of piperidine gradually added, cooling with water all the time. As soon as the liquid began to thicken, alcohol was added; this prevented the whole from setting to a hard cake, as in Knoevenagel's experiment. The compound is deposited from the solution in a crystalline condition, and after recrystallisation from alcohol, forms colourless needles melting constantly at 92.5° , showing straight extinction in polarised light and giving no coloration with ferric chloride. (Knoevenagel gives the melting point as 86° , but he employed only 2 grams of ethyl benzoylacetate in the preparation of the substance, and the quantity obtained was probably insufficient for complete purification. He does not indicate the crystalline form.)

The yield varied somewhat. The most favourable result was 100 grams of once crystallised product from the foregoing quantities.

Wislicenus and Kuhn (*Annalen*, 1898, 302, 215) prepared ethyl dibenzoylglutarate by the action of methylene diiodide on ethyl benzoylsodioacetate. In this way, they obtained it as an uncrystallisable oil, which gave a cherry-red coloration with ferric chloride.† In one experiment, they obtained an isomeric ethyl dibenzoylglutarate melting at 130.5° .

Preparation of $\alpha\gamma$ -Dibenzoylpropane,

—Wislicenus and Kuhn prepared this compound by boiling the "crude, oily ethyl dibenzoylglutarate" with a 10 per cent. aqueous solution of potassium hydroxide for 9 hours. This process, however, yielded, along with the diketone, γ -benzoylbutyric acid. In order to

* This was done merely because we happened to have a stock of the former base. In many of these condensations, Knoevenagel uses either base indifferently.

† This coloration may, of course, have been due to an enolic form of ethyl dibenzoylglutarate. Still, some proof of the absence of unchanged ethyl benzoylacetate from the uncrystallisable oil would appear desirable.

avoid this "acid hydrolysis," we hydrolysed the ester by boiling it with dilute sulphuric acid.

Forty grams of crystallised ethyl dibenzoylglutarate were boiled for 2 hours with 200 c.c. of a mixture of equal volumes of concentrated sulphuric acid and water, using a reflux condenser. A more dilute acid does not produce hydrolysis, whilst one more concentrated completely resinifies the substance; indeed, even with an acid of the foregoing strength there is a certain amount of resinification, the organic substance, which floats in a fused condition on the surface of the liquid, being reddish-brown at the end of the process, whilst the aqueous layer is highly fluorescent. The evolution of carbon dioxide is practically complete at the end of the 2 hours, and longer boiling diminishes the yield. The flask was cooled with water, shaking all the time, and the product, which was thus obtained in a granular form, was separated, washed with water, dissolved in ether, and the ethereal solution was shaken with sodium carbonate solution, dried with calcium chloride, and concentrated. The dibenzoylpropane was deposited in lustrous laminae, a second crystallisation sufficing to furnish a colourless product melting at 67.5° , as described by Wislicenus and Kuhn. From alcohol, it crystallises in blades; from light petroleum, in which it is only sparingly soluble, in very slender needles. The yield was 65 per cent. of the theoretical.

Reduction of Dibenzoylpropane in Ethereal solution with Sodium.—The process of reduction was carried out exactly as prescribed by Wislicenus and Kuhn (*loc. cit.*, 221). An ethereal solution of 10 grams of dibenzoylpropane was introduced into a flask along with water, and 40 grams of sodium in small pieces was gradually added, cooling all the time. (Wislicenus and Kuhn merely state that a very large excess of sodium is to be employed, without specifying the amount.) The addition of the sodium took about 2 days. The ethereal solution was separated from the yellow, aqueous layer, dried with anhydrous sodium sulphate, and evaporated to expel the ether, after which it was left in a vacuum desiccator over sulphuric acid for several days. It formed a pale yellow syrup, agreeing with the description given by Wislicenus and Kuhn, who analysed it in this condition.

As our final results in dealing with this substance differ very materially from those of Wislicenus and Kuhn, we venture to describe the method of purification more fully than would otherwise be necessary.

The syrupy substance was extracted with successive portions of boiling light petroleum ("ligroin"), using a reflux condenser; it became crystalline on warming with the light petroleum, but the crystals afterwards melted again. After four extractions there remained only a hard, yellow resin, insoluble in light petroleum. The four extracts,

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which were kept separate, deposited on cooling a colourless oil, which on standing partly crystallised in short, *thickish* needles, which give a *red* coloration with concentrated sulphuric acid. The first extract yielded most crystals. The united mother liquors from these crops gave on concentration tufts of *very slender* needles, totally distinct from the others. After recrystallisation from light petroleum they melted at 84—88°, and when free from the thickish needles gave only a *yellow* coloration with sulphuric acid. They proved to be $\alpha\epsilon$ -*diphenyl- $\alpha\epsilon$ -dihydroxypentane* described later on. The last mother liquor gave a small quantity of unaltered dibenzoylpropane.

The purification of the substance crystallising in thickish needles was a matter of some difficulty owing to the oil with which they were contaminated. In the case of the first crop some fairly pure substance was obtained by recrystallising from a mixture of benzene and light petroleum. The other portions were dissolved in boiling light petroleum, and the flask containing the decanted hot solution shaken under the tap until a portion of the oil had separated; the solution, again decanted from the oil, gave the short, thickish, prismatic needles. The various portions of crystalline substance obtained by these various methods were finally united and recrystallised from light petroleum until they showed the constant melting point of 103—104·5°. In polarised light, the needles show oblique extinction. They dissolve in concentrated sulphuric acid, giving a deep red, strongly fluorescent solution. Owing to loss in purification, the yield of pure substance was only 1·4 grams.

Occasionally in the crystallisation of the foregoing substance the tufts of slender needles (m. p. 84—88°) made their appearance. These could be got rid of by pouring off the solution from the thickish needles before the others separated.

After both kinds of crystals had been as far as possible removed, there remained a colourless oil which could not be made to crystallise by contact with any of the three crystalline substances isolated from the mixture. It was not further examined.

Analysis of the substance melting at 103—104·5° gave figures agreeing with those required by the cyclic pinacone, 1 : 2-*diphenyl-1 : 2-dihydroxycyclopentane*,

0·1652 gave 0·4846 CO₂ and 0·1059 H₂O. C = 80·00; H = 7·12.

C₁₇H₁₈O₂ requires C = 80·31; H = 7·08 per cent.

Afterwards, when we had prepared the cyclic pinacone in quantity by the reduction of dibenzoylpropane with aluminium amalgam, we found that it was deposited from glacial acetic acid in crystals of the

formula $C_{17}H_{18}O_2, C_2H_4O_2$ sparingly soluble in the cold acid. The pinacone should be dissolved in the glacial acetic acid with the aid of a gentle warmth, as heating with the acid turns it yellow, and decomposes it. In the form of this double compound the pinacone can, as the following experiment shows, be readily separated from the other substances formed in Wislicenus and Kuhn's process of reduction.

Ten grams of dibenzoylpropane in ethereal solution were again reduced with sodium as already described, but instead of treating the syrupy product with light petroleum, it was dissolved in a little more than its own bulk of glacial acetic acid. As it showed no tendency to crystallise, a small portion was removed and frozen with ice and salt; on allowing it to thaw, crystals of the double compound remained, and with these the crystallisation of the rest was started. The substance was deposited in large crystals; after expelling the acetic acid of crystallisation, the pinacone thus obtained weighed 3.7 grams, and, save for a very faint brownish tinge, was pure. After a second crystallisation from acetic acid, it was colourless. The crystals effloresce only very slowly at the ordinary temperature. For analysis, they were dried by pressing between filter paper and then exposing to the air for two and a half hours.

0.8735 lost, on heating at 70° , 0.1688. $C_2H_4O_2 = 19.32$.

$C_{17}H_{18}O_2, C_2H_4O_2$ requires $C_2H_4O_2 = 19.10$ per cent.

The acetic acid mother liquor, separated from the first crop of crystals of the foregoing double compound and containing the remainder of the reduction product, yielded, by spontaneous evaporation, only a small quantity of the same crystals, imbedded, however, in a thick syrup which showed no tendency to crystallise. We estimate that the crude, syrupy reduction compound, analysed as the cyclic pinacone by Wislicenus and Kuhn, contains not more than 50 per cent. of that substance.

Reduction of Dibenzoylpropane with Sodium in boiling Alcohol.—

Twenty grams of dibenzoylpropane were dissolved in absolute alcohol and 24 grams of sodium gradually added to the boiling solution. On diluting with water, an oil separated; this was taken up with ether, the ethereal solution dried with fused potassium carbonate, and the ether expelled on the water-bath. The yellow, oily product showed no tendency to crystallise, but by the following rather tedious process we succeeded in isolating a crystalline substance from it. The oil was dissolved in a moderate bulk of alcohol; the solution was diluted with an equal volume of water, shaken in a corked flask, and allowed to stand. As soon as the oil had settled, the solution, which was still somewhat turbid, was decanted into a beaker and again allowed to

stand, so as to allow part of the alcohol to evaporate. More oil separated, and the liquid, which had become clear, was again decanted and allowed to evaporate in a vacuum desiccator over sulphuric acid, when it deposited clear, prismatic crystals.* The oils were redissolved in alcohol and again treated in the same way, repeating the process as often as crystals were obtained. The united crops of crystals were recrystallised, once from dilute alcohol by the same method, and then twice from light petroleum. From the latter solvent, the substance was deposited in very slender needles melting at $84-88^\circ$, identical with those obtained in small quantity along with 1:2-diphenyl-1:2-dihydroxycyclopentane in the treatment of Wislicenus and Kuhn's reduction product with light petroleum. In the present case, if the crystallisation was allowed to go on too long, a slight separation of the thickish, short needles of the cyclic pinacone from the light petroleum solution was observed, but by filtering as soon as the slender needles were deposited, the pinacone remained in the mother liquor.

The new compound crystallises from dilute alcohol in lustrous, slender, six-sided prisms, from light petroleum in very slender needles, both showing straight extinction in polarised light. The melting point is not sharp; the substance fuses between $84-88^\circ$ to a turbid liquid which clears at 92° . If free from the cyclic pinacone, it gives only a yellow coloration with concentrated sulphuric acid.

Analysis gave figures agreeing with the formula of $\alpha\epsilon$ -diphenyl- $\alpha\epsilon$ -dihydroxypentane, $C_6H_5 \cdot CH(OH) \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH(OH) \cdot C_6H_5$.

0.1314 gave 0.3817 CO_2 and 0.0926 H_2O . C = 79.22; H = 7.83.

0.1356 ,, 0.3953 CO_2 ,, 0.0951 H_2O . C = 79.50; H = 7.79.

$C_{17}H_{20}O_2$ requires C = 79.69; H = 7.81 per cent.

The yield of pure substance from 20 grams of dibenzoylpropane was only 0.3 gram.

Reduction of Dibenzoylpropane by Aluminium Amalgam.—This reaction furnishes the best means of obtaining 1:2-diphenyl-1:2-dihydroxycyclopentane, but the success of the method depends on the observance of certain precautions. No reduction takes place in absolute alcohol; the best result was obtained with a solution in alcohol diluted with half its volume of water. The condition of the amalgam is important; if it is allowed to heat up and oxidise during its preparation, it becomes inert. The following method gave a good result.

Ten grams of aluminium powder, previously freed from oil by treatment with ether in a Soxhlet's extractor, was shaken for a few seconds with 10 c.c. of a saturated alcoholic solution of mercuric chloride

* Sometimes an oil separates at this point also, and does not crystallise until after long standing. Once crystals have been obtained, it is better to start the crystallisation with nuclei of these.

which had been diluted with 100 c.c. of the same solvent, was then rapidly filtered through a disc of loose felt on a perforated porcelain funnel, using the filter pump, washed quickly with alcohol, and at once transferred to a flask containing 10 grams of dibenzoylpropane, 200 c.c. of alcohol, and 100 c.c. of water. The flask was fitted with a condensing tube and was heated on a metal plate over the water-bath, repeating the heating every day for some time. At first the liquid deposited, on cooling overnight, blades of dibenzoylpropane, the quantity of which, however, daily diminished, until at last they ceased to appear. The reduction must, however, be carried considerably beyond this point. After a week, as the evolution of hydrogen had become very slow, a second portion of 10 grams of aluminium amalgam was added, and a third was sometimes found necessary at the end of another week. From a fortnight to three weeks' heating was thus required according to the activity of the amalgam, and it was found that the addition of the latter in successive portions, as just described, gave a better result than when it was added all at once. The filtered and concentrated solution ought to yield, on diluting slightly with water, needles of the cyclic pinacone, unmixed with the blades and laminae of unaltered dibenzoylpropane. If, however, the latter substance is present, the mixture of crystals should be dissolved in a little glacial acetic acid with the aid of a gentle warmth; the liquid on standing deposits crystals of the cyclic pinacone containing acetic acid of crystallisation, whilst the dibenzoylpropane remains in solution. If it is necessary to concentrate this solution, it should be done under diminished pressure, in order to avoid the decomposing action of the hot acid on the pinacone.

If the reduction has been properly carried out, the yield is quantitative.

The pinacone was deposited from dilute alcohol in thick needles. For analysis, it was recrystallised from light petroleum, from which it separated in short needles melting at $103-104.5^{\circ}$, identical with the compound of the same melting point obtained by the reduction of dibenzoylpropane with sodium in ethereal solution. Analysis gave figures agreeing with those required by 1:2-diphenyl-1:2-dihydroxycyclopentane.

0.1816 gave 0.5340 CO_2 and 0.1190 H_2O . C = 80.19; H = 7.28.

0.1511 „ 0.4440 CO_2 „ 0.0965 H_2O . C = 80.13; H = 7.09.

$\text{C}_{17}\text{H}_{18}\text{O}_2$ requires C = 80.31; H = 7.08.

Stereoisomerides were not observed.

Oxidation of 1:2-Dibenzoyl-1:2-diphenylcyclopentane to $\alpha\gamma$ -Dibenzoylpropane.—1.5 grams of the cyclic pinacone were dissolved in glacial acetic acid with the aid of a gentle warmth, and the same weight of

chromium trioxide, dissolved in the same menstruum, was gradually added. As no oxidation had taken place after standing for 20 hours in the cold, the mixture was warmed for a short time on the water-bath and then poured into water. Laminæ of $\alpha\gamma$ -dibenzoylpropane separated. After freeing from acid by means of sodium carbonate, an ethereal solution deposited crystals showing the melting point of $\alpha\gamma$ -dibenzoylpropane (67.5°) and indistinguishable from that substance.

Reduction of 1 : 2-Dibenzoyl-1 : 2-diphenylcyclopentane with Hydriodic Acid and Red Phosphorus.—This reduction was carried out exactly as described by Wislicenus and Kuhn, heating the cyclic pinacone with hydriodic acid and red phosphorus in sealed tubes at 150 — 160° . One set of experiments was performed with the crude syrupy pinacone, as prescribed by these authors. Afterwards we used the pure pinacone. Finally we tried the experiment, not mentioned by Wislicenus and Kuhn, of boiling *dibenzoylpropane* with hydriodic acid (sp. gr. 1.7) and red phosphorus for 13 hours.

In every case, by employing the method of purification prescribed by these authors—namely, of repeatedly dissolving the product of reduction in ether and precipitating it with alcohol—we obtained what appeared to be the same substance. It was a white, wax-like solid, which showed a tendency to become more granular by repeated precipitation and which finally melted at 105 — 108° . It was readily soluble in ether and in benzene, practically insoluble in alcohol. In these respects it agreed fairly well with the description of Wislicenus and Kuhn's hydrocarbon melting at 108° .

We introduced a portion of this product (prepared from the syrupy pinacone) into a bulb which was exhausted by means of a filter-pump and then heated in a spermaceti-bath, the temperature being gradually raised to 340° . At that temperature and under a pressure of 12 mm., there was a mere trace of a distillate, but the greater part of the substance showed no sign of volatilising. The distillate did not crystallise.

We had intended to make an ebullioscopic determination of the molecular weight of the substance, but after the result of the foregoing experiment, we did not regard this as necessary. The molecular weight was obviously very much higher than that of a diphenylcyclopentane—the substance which Wislicenus and Kuhn had supposed it to be.

The mother liquors obtained in the purification of the foregoing substance were examined. By evaporating to dryness and distilling the residue under diminished pressure a crystalline substance was obtained, but in quantity too small for further examination. It was not identical with Japp and Burton's 1 : 2-diphenylcyclopentane (m. p. 47°). The latter compound is not formed in this reduction.

Boiling point of 1:2-Diphenylcyclopentane (m. p. 47°) from *Anhydracetonebenzil*.—Japp and Burton (Trans., 1887, 51, 423) found that, under atmospheric pressure, this hydrocarbon boils, with partial decomposition, at 305°. In order better to compare it with Wislicenus and Kuhn's supposed 1:2-diphenylcyclopentane, we determined its boiling point under reduced pressure. A well-crystallised specimen melting at 47° was employed for the purpose. It passed over without decomposition quite constantly at 189° under 12 mm. pressure (temperature of oil-bath 200°). The colourless distillate solidified to a mass of white crystals of unchanged substance.

Oxidation of 1:2-Diphenylcyclopentane (m. p. 47°).—0.6 gram of 1:2-diphenylcyclopentane (m. p. 47°) was dissolved in glacial acetic acid, a solution of 1.2 grams of chromium trioxide in acetic acid was gradually added, the mixture was allowed to stand for 20 hours, and poured into water. Solid caustic soda was added so as to leave the liquid slightly acid, after which the solution was extracted with ether. The ethereal solution, after removing acids, deposited laminae of *αγ-dibenzoylpropane*, which after recrystallisation showed the correct melting point of 67.5°. A supersaturated solution of the substance in alcohol at once crystallised on seeding it with a crystal of dibenzoylpropane.

Benzoic acid was also formed, together with a small quantity of an acid crystallising from water in minute prisms or needles melting at 133.5°, which we were unable to identify.

Reduction of Diphenyldibenzoylbutadiene.—Five grams of diphenyldibenzoylbutadiene were boiled with 200 grams of glacial acetic acid, 10 grams of hydriodic acid (sp. gr. 1.7), and 2 grams of red phosphorus for 3½ hours, employing a reflux condenser. The liquid was filtered, precipitated with water, and extracted with ether; the ethereal solution was treated with sulphurous acid and sodium carbonate, dried with calcium chloride, and after expelling the ether, the residue was distilled under a pressure of 12 mm. Part passed over at 80–85°; it smelt of acetophenone, and when cooled in melting ice and touched with a small crystal of acetophenone, solidified. Nearly the whole of the residue distilled when the oil-bath was at 275–295°. It was dissolved in alcohol. On cooling, an oil separated. The mother liquor was evaporated to a small bulk and crystallisation was started by seeding with 2:3:5-triphenylfurfuran. The oils were repeatedly boiled up with alcohol and the clear solutions obtained on cooling were treated in the same manner. In this way, a relatively good yield of colourless needles was obtained. After recrystallisation they melted at 92–93°, were indistinguishable from crystals of 2:3:5-triphenylfurfuran (m. p. 92–93°) and, like these, showed straight extinction in polarised light. Wislicenus and Lehmann obtained in the analysis

of this substance: $C=88.85$, $H=5.60$ (mean of two analyses), the formula of triphenylfurfuran, $C_{22}H_{16}O$, requiring $C=89.19$, $H=5.40$. The formula $C_{20}H_{14}O$, calculated by Wislicenus and Lehmann, requires $C=88.88$, $H=5.20$, so that analysis alone is hardly competent to decide between the two formulæ. The proof of the correctness of the formula $C_{22}H_{16}O$ is to be found in the fact that the same compound is formed in a quantitative yield by the reduction of $\alpha\beta$ -dibenzoylphenylethylene and by other methods which leave no doubt as to its constitution. The above experiment shows, moreover, that the treatment of the product of the reduction of diphenyldibenzoylbutadiene with alcoholic potash, which Wislicenus and Lehmann regarded as essential to the formation of the substance melting at $92-23^{\circ}$, was unnecessary.

The chief products of the reduction of diphenyldibenzoylbutadiene in our experiment were, therefore, *acetophenone*, formed by hydrolysis, and *2:3:5-triphenylfurfuran*, formed by the reduction of $\alpha\beta$ -dibenzoylphenylethylene, the other product of hydrolysis (see Introduction).

The other compounds obtained by Wislicenus and Lehmann may have been present in the residue, sparingly soluble in alcohol, which remained after the extraction of the triphenylfurfuran; but we did not examine this further.

CHEMICAL DEPARTMENT,
UNIVERSITY OF ABERDEEN.