CVIII.—*Homologues of Anhydracetonebenzil.*

By FRANCIS R. JAPP, F.R.S., and ANDREW N. MELDRUM, B.Sc.

ANHYDRACETONEBENZIL, one of the products of the condensation of benzil with acetone under the influence of potassium hydroxide, was shown by Japp and Lander (*Trans.*, 1897, 71, 123) to be a *diphenyl-*

cyclopentenolone of the formula
$$\begin{array}{c} \text{C}_6\text{H}_5 \cdot \text{C} = \text{CH} \\ | \\ \text{C}_6\text{H}_5 \cdot \text{C}(\text{OH}) \cdot \text{CH}_2 \end{array} > \text{CO}.$$

By the condensation of benzil with homologues of acetone of the general formulæ $\text{CH}_2\text{R}' \cdot \text{CO} \cdot \text{CH}_3$ and $\text{CH}_2\text{R}' \cdot \text{CO} \cdot \text{CH}_2\text{R}'$, Japp and Burton (*Trans.*, 1887, 51, 431) prepared various homologues of anhydracetonebenzil. The constitution of those members of this class which are formed from symmetrical homologues of acetone follows, as a matter of course, from that of anhydracetonebenzil itself; thus the condensation product of benzil with diethyl ketone (*loc. cit.*, p. 432) is

$\alpha\beta$ -dimethylanhydracetonebenzil,
$$\begin{array}{c} \text{C}_6\text{H}_5 \cdot \text{C} = \text{C}(\text{CH}_3) \\ | \\ \text{C}_6\text{H}_5 \cdot \text{C}(\text{OH}) \cdot \text{CH}(\text{CH}_3) \end{array} > \text{CO} \quad (\text{m. p.}$$

150°), if we distinguish the CH group in the pentacarbon ring of anhydracetonebenzil as the α -, and the CH₂ group as the β -position (compare *Trans.*, 1899, 75, 1019). But in the case of the compounds obtained from unsymmetrical homologues of acetone, there are two possibilities; thus, from benzil and methyl ethyl ketone both the α - and the β -methyl derivative may be obtained:

Japp and Lander (*loc. cit.*, p. 129) found that α -derivatives are more stable towards permanganate in the cold than β -derivatives, and in this way arrived at the conclusion that the monoalkyl derivatives of anhydracetonebenzil obtained by Japp and Burton belonged to the β -class.* This conclusion was confirmed by Japp and Findlay, who found that these compounds did not interact with benzaldehyde to yield benzylidene derivatives, whereas anhydracetonebenzil compounds containing the methylene group readily do so.

We have now repeated and largely extended Japp and Burton's work.

Their method of preparing these compounds (*loc. cit.*, p. 431) consisted in warming a mixture of the ketone in question—thus methyl ethyl ketone—and benzil with aqueous potassium hydroxide for some days at a temperature of 20—25°. This procedure left unchanged a considerable amount of benzil, which had to be removed by washing the product with ether. We find that in this way a soluble isomeride was removed along with the benzil, and overlooked. By using a slight excess of the ketone and heating to a somewhat higher temperature, we ensure the total conversion of the benzil. The separation of the two isomerides then presents no difficulty.

In the foregoing mode of preparation, the sparingly soluble isomeride generally predominates; but we find that, by allowing the condensation of the ketone with benzil to take place at the ordinary temperature in a 0·5 per cent. solution of potassium hydroxide in absolute alcohol, the more soluble isomeride is generally formed in greater quantity.

* Although this conclusion happened to be correct, we have since convinced ourselves that, except in the case of acid derivatives of anhydracetonebenzil, which may be dissolved in a solution of sodium carbonate before applying the permanganate test, the difference in the rate of oxidation is not sufficiently marked to serve as a means of distinguishing with certainty between the two classes. The open-chain condensation compounds of benzil with ketones may, however, be distinguished from anhydracetonebenzil derivatives by the much greater ease with which they are attacked by permanganate.

In the case of the monoalkyl anhydracetonebenzils, the α -compounds are more soluble, and melt lower, than the corresponding β -compounds.

In the condensation of benzil with methyl ethyl ketone, there is formed, in addition to α -methylanhydracetonebenzil (m. p. 118°) and β -methylanhydracetonebenzil (m. p. 180.5°), a third isomeride melting at 157° . Its formation was only once observed in the original condensation, but it can be prepared from the β -compound by leaving the latter for a month in contact with cold alcoholic 0.5 per cent. potassium hydroxide, or by boiling it with glacial acetic acid. In both cases, the transformation is only partial, and, moreover, the resulting compound is partially retransformed into β -methylanhydracetonebenzil by allowing it to stand with alcoholic potassium hydroxide in the cold, so that there is evidently an equilibrium. By heating alone at 330° , it is totally converted into β -methylanhydracetonebenzil. We regard this compound as *desylene-methyl ethyl ketone*—probably the fumaroid

form,
$$\begin{array}{c} \text{C}_6\text{H}_5 \quad \text{CO} \cdot \text{CH}_2 \cdot \text{CH}_3 \\ | \quad \quad | \\ \text{C} = \text{C} \\ | \quad \quad | \\ \text{C}_6\text{H}_5 \cdot \text{CO} \quad \text{H} \end{array}$$
 . In its transformation into β -methylanhydracetonebenzil, it would first pass into the maleoid form, which would then undergo internal aldol condensation :

That this compound is not a stereoisomeride of β -methylanhydracetonebenzil is, we consider, proved by the fact that it is so much more readily attacked by permanganate than the latter compound. The substance is, however, difficult to obtain in quantity, so that we have not been able to make a detailed study of its reactions, and we therefore put forward the above formula with reserve.

A similar open-chain isomeride of $\alpha\beta$ -dimethylanhydracetonebenzil is described later on.

By boiling either α - or β -methylanhydracetonebenzil for a few minutes with fuming hydriodic acid, *methyl diphenylcyclopentenone*,
$$\begin{array}{c} \text{C}_6\text{H}_5 \cdot \text{C} \cdot \text{CH}(\text{CH}_3) \\ | \quad \quad | \\ \text{C}_6\text{H}_5 \cdot \text{C} \text{---} \text{CH}_2 \end{array} \text{CO}$$
 (m. p. $77\text{--}78^\circ$), was obtained. It yields a phenylhydrazone. The same migration of the double bonds occurs during the reduction as in the formation of diphenylcyclopentenone,
$$\begin{array}{c} \text{C}_6\text{H}_5 \cdot \text{C} \cdot \text{CH}_2 \\ | \quad \quad | \\ \text{C}_6\text{H}_5 \cdot \text{C} \cdot \text{CH}_2 \end{array} \text{CO}$$
, from anhydracetonebenzil. The symmetrical con-

stitution of the latter *cyclopentenone* was proved by Japp and Lander (Trans., 1897, **71**, 132) by oxidising it to diphenylmaleic acid.

By boiling α -methylanhydracetonebenzil for 5 hours with hydriodic acid and red phosphorus, it was completely reduced to 1-methyl-2:3-diphenylcyclopentane, $\text{C}_6\text{H}_5 \cdot \text{CH} \cdot \text{CH}(\text{CH}_3) \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_5$ (m. p. 62–63°), already obtained by Japp and Murray (Trans., 1897, **71**, 152), by the reduction of α -anhydracetonebenzillævulic acid, the carboxyl group of the acid being eliminated in the latter case.

α -Methylanhydracetonebenzil, like anhydracetonebenzil itself, readily interacts with benzaldehyde under the influence of alcoholic potassium hydroxide in the cold, yielding a benzylidene derivative. *Benzylidene- α -methylanhydracetonebenzil* (m. p. 225°) has the constitution

The other α -alkylanhydracetonebenzils yield similar benzylidene derivatives.

When β -methylanhydracetonebenzil, on the other hand, is allowed to stand with benzaldehyde and alcoholic potassium hydroxide, there is, at first, apparently no action. After the mixture has stood for a month, however, it is found that a portion of the β -methylanhydracetonebenzil has been converted into the open-chain compound desylene-methyl ethyl ketone* (m. p. 157°) already referred to, whilst a very small quantity of the benzylidene derivative of α -methylanhydracetonebenzil has been formed. This means that, in presence of the potassium hydroxide, a portion of the β -methylanhydracetonebenzil is hydrolysed to benzil and methyl ethyl ketone (the formation of the open-chain compound being an intermediate stage), and that these products of hydrolysis again interact, yielding, in part at least, α -methylanhydracetonebenzil, which then undergoes condensation with the benzaldehyde.

α -Methylanhydracetonebenzil and benzil interact, in presence of alcoholic potassium hydroxide, to form *α -methylanhydracetonedibenzil*, $\text{C}_{32}\text{H}_{26}\text{O}_4$ (dimorphous; silky needles, m. p. 185°; and warty crystals, m. p. 194°),

which is obtained in the form of the complex *potassium salt*, $\text{C}_{32}\text{H}_{25}\text{O}_4\text{K} \cdot \text{C}_{32}\text{H}_{26}\text{O}_4 \cdot 4\text{C}_2\text{H}_5 \cdot \text{OH}$. From this salt, the free substance is obtained by treating it with acetic acid. α -Methylanhydracetonedibenzil

* We at first took this substance for an aldol condensation compound of benzaldehyde with β -methylanhydracetonebenzil (see Trans., 1899, **76**, 1020, footnote). The difference in percentage composition is but small.

benzil may be more simply prepared by the action of an alcoholic solution of sodium ethoxide on a mixture of benzil (2 mols.) with methyl ethyl ketone (1 mol.):

the substance being thus obtained in the form of its *sodium* salt. When α -methylanhydracetonedibenzil is boiled with alcohol containing a few drops of sulphuric acid, it is esterified, yielding the compound $\text{C}_{32}\text{H}_{25}(\text{OC}_2\text{H}_5)\text{O}_8$ (m. p. 250°). In yielding salts with caustic alkalis, and in being esterified under the foregoing conditions, α -methylanhydracetonedibenzil resembles ethyl anhydrodibenzilacetoacetate (Japp and Lander, Trans., 1896, 69, 736), and differs entirely from the corresponding compound from acetone and benzil—*anhydracetonedibenzil*, $\text{C}_{31}\text{H}_{24}\text{O}_4$ —of which it might otherwise appear to be the next higher homologue.

By boiling α -methylanhydracetonebenzil with sulphuric acid somewhat diluted with water, or with glacial acetic acid, a dehydration product, $\text{C}_{36}\text{H}_{28}\text{O}_2$ (m. p. 230° , with evolution of gas), is formed according to the equation

The molecular weight of the resulting compound is doubled in order to bring it into line with the corresponding compound, $\text{C}_{24}\text{H}_{24}\text{O}_2$, from anhydracetonebenzil (Japp and Lander, Trans., 1897, 71, 131). β -Methylanhydracetonebenzil is converted into the same dehydration product, $\text{C}_{36}\text{H}_{28}\text{O}_2$, by heating it in a sealed tube with anhydrous formic acid; whereas glacial acetic acid, as already mentioned, transforms it into desylene-methyl ethyl ketone.

EXPERIMENTAL.

Condensation of Benzil with Methyl Ethyl Ketone.

Preparation of α -Methylanhydracetonebenzil, $\begin{array}{c} \text{C}_6\text{H}_5 \cdot \text{C} = \text{C}(\text{CH}_3) \\ | \\ \text{C}_6\text{H}_5 \cdot \text{C}(\text{OH}) \cdot \text{CH}_2 \end{array} > \text{CO},$
and β -Methylanhydracetonebenzil, $\begin{array}{c} \text{C}_6\text{H}_5 \cdot \text{C} = \text{CH} \\ | \\ \text{C}_6\text{H}_5 \cdot \text{C}(\text{OH}) \cdot \text{CH}(\text{CH}_3) \end{array} > \text{CO}.$ —These compounds are formed by the condensation of benzil with methyl ethyl ketone under the influence of potassium hydroxide. With alcoholic potassium hydroxide, the α -compound is almost the sole product; with aqueous potassium hydroxide, the β -compound slightly predominates.

In the preparation of the α -compound, 10 grams of finely powdered benzil, 7 grams of methyl ethyl ketone, and 100 c.c. of alcoholic 0.5

per cent. potassium hydroxide (4 grams KOH to 1 litre of absolute alcohol *) were introduced into a flask which was then corked and, after dissolving the benzil by shaking, allowed to stand. The experiment was so arranged that the liquid nearly filled the flask and that the quantity of alcohol was just sufficient to dissolve the benzil. After standing at the ordinary temperature for 17 days, the liquid, from which nothing had been deposited, was poured into a large bulk of water; this occasioned the separation of an oil, which speedily solidified to a mass of almost white crystals of the α -compound. After a single crystallisation from hot alcohol, the substance was pure. It formed large, flat, lozenge-shaped crystals melting at 118° . It is readily soluble both in alcohol and in ether.

Analysis of α -methylanthracetonebenzil gave figures agreeing with the formula $C_{18}H_{16}O_2$:

0.1585 gave 0.4734 CO_2 and 0.0866 H_2O . C = 81.47; H = 6.07.

0.1402 „ 0.4187 CO_2 „ 0.0781 H_2O . C = 81.45; H = 6.19.

$C_{18}H_{16}O_2$ requires C = 81.82; H = 6.06 per cent.

The yield from the above quantities was 8 grams, and the alcoholic mother liquor gave a small amount—considerably less than a gram—of the isomeric β -methylanthracetonebenzil already obtained by Japp and Burton.

In order to prepare β -methylanthracetonebenzil in quantity, the method employed by Japp and Burton (*loc. cit.*) was, with slight modifications, adopted. Forty grams of benzil, 25 grams of methyl ethyl ketone, and 30 c.c. of aqueous potassium hydroxide of 33.3 per cent. strength were introduced into a conical flask fitted with a condensing tube, the whole being placed on a metal plate over a water-bath and heated for 9 hours, shaking from time to time. The mixture, which had become brown, was poured into excess of hot water. The solidified substance was ground, washed with water, and well extracted with cold ether. The residue was dissolved in boiling alcohol; on cooling, prismatic crystals of β -methylanthracetonebenzil were deposited, which, after two or three recrystallisations, melted constantly at 180° (179° , Japp and Burton). The alcoholic mother liquor gave a small quantity of octahedral crystals melting at 157° , of a substance which is isomeric with the two foregoing, and which we regard as desylene-methyl ethyl ketone (*v. infra*). The ethereal extract gave a considerable quantity of α -methylanthracetonebenzil (m. p. 118°).

In the foregoing experiment, the quantity of α -compound obtained

* Absolute alcohol should be used in these condensations. "Methylated spirit" (alcohol "denatured" with crude wood spirit; compare *Trans.*, 1897, **71**, 297, footnote) must be avoided, as it contains acetone, which yields condensation compounds of its own with benzil.

was 8.5 grams, and of β -compound, 11 grams. Longer heating diminished the proportion of the β -compound, and in addition, the resinous bye-products rendered the substances more difficult to purify.

β -Methylanhydracetonebenzil has already been analysed by Japp and Burton.

Molecular Weights of α - and β -Methylanhydracetonebenzil.—The molecular weights of the two compounds were determined by Walker and Lumsden's modification of Landsberger's ebullioscopic method, using alcohol (constant = 1560) as a solvent.

α -Methylanhydracetonebenzil.

Substance.	Elevation.	Volume.	Mol. wt.
0.908	0.32°	16.6 c.c.	267.
„	0.24	22.4 „	263.
$C_{18}H_{16}O_2 = 264.$			

β -Methylanhydracetonebenzil.

0.896	0.292°	15.6 c.c.	308.
„	0.210	22.2 „	300.
$C_{18}H_{16}O_2 = 264.$			

The two substances are therefore isomeric.

Benzylidene- α -methylanhydracetonebenzil, $C_6H_5 \cdot \overset{\cdot}{C} : C(CH_3) > CO$
 $C_6H_5 \cdot \overset{\cdot}{C}(OH) - C = CH \cdot C_6H_5$

—Five grams of α -methylanhydracetonebenzil, 2.5 grams of benzaldehyde, and 65 c.c. of alcoholic potassium hydroxide (0.5 per cent.) were mixed, shaken until all had dissolved, and allowed to stand. Overnight, tufts of needle-shaped crystals had formed; after 4 days they were separated and recrystallised from hot glacial acetic acid, from which the substance was deposited in colourless, slender, rectangular prisms melting at 225°. (Yield 3.6 grams.)

0.1608 gave 0.5018 CO_2 and 0.0839 H_2O . C = 85.11; H = 5.80.

$C_{25}H_{20}O_2$ requires C = 85.23; H = 5.68 per cent.

β -Methylanhydracetonebenzil, when subjected to the above treatment for the same time, is quite unchanged. Its behaviour on long standing with the mixture is mentioned in the introduction.

Conversion of β -Methylanhydracetonebenzil into Desylene-methyl Ethyl

Ketone, $C_6H_5 \cdot \overset{\cdot}{C} : CH \cdot CO \cdot C_2H_5$.—The best mode of effecting this trans-

formation is by boiling β -methylanhydracetonebenzil with four times its weight of glacial acetic acid for 4 hours. The solution, on cooling, deposits needles or prisms of unchanged substance; and from the

mother liquor, octahedral crystals of the open-chain compound, melting at 157° , may be obtained.

The same compound is also slowly formed when finely powdered β -methylanhydracetonebenzil is allowed to stand for a month or more with alcoholic potassium hydroxide (0.5 KOH per cent.) insufficient to dissolve it. The transformation is incomplete, as the reaction is reversible (see introduction).

The formation of the same compound was also observed in the preparation of β -methylanhydracetonebenzil (*v. supra*).

Analysis of the octahedral crystals (m. p. 157°) showed that the substance, which we regard as *desylene-methyl ethyl ketone*, is isomeric with α - and β -methylanhydracetonebenzil.

0.1485 gave 0.4431 CO_2 and 0.0798 H_2O . C = 81.36 ; H = 5.97.

0.1629 „ 0.4862 CO_2 „ 0.0903 H_2O . C = 81.39 ; H = 6.16.

$\text{C}_{18}\text{H}_{16}\text{O}_2$ requires C = 81.82 ; H = 6.06 per cent.

The reason for regarding this compound as structurally different from the methylanhydracetonebenzils is that it is much more readily attacked by permanganate.

A small quantity of the compound was heated in an exhausted tube for a short time at 330° . There was no sign of decomposition, and the melted substance began to distil and collect in the cooler part of the tube. On crystallising the product from alcohol, it was found that it had been re-converted into β -methylanhydracetonebenzil (m. p. 180°).

α -Methylanhydracetonebenzil is quite unchanged by contact with alcoholic potassium hydroxide of the above strength. Boiling with glacial acetic acid dehydrates it, yielding the compound, $\text{C}_{36}\text{O}_{28}\text{O}_2$, melting at 230° (*v. infra*).

Action of Dehydrating Agents on α - and β -Methylanhydracetonebenzil.—One gram of α -methylanhydracetonebenzil was boiled for half-an-hour with 5 c.c. of sulphuric acid diluted with 10 c.c. of water, employing a reflux condenser. From the product, which was very dark coloured, crystals melting at 230° were obtained. The following method yields the substance in a purer state.

One gram of α -methylanhydracetonebenzil was boiled with 4 grams of glacial acetic acid for 4 hours. On cooling, the liquid deposited a crystalline compound which proved to be identical with that obtained by the action of hot dilute sulphuric acid. Recrystallised, first from glacial acetic acid and afterwards from amyl alcohol, it formed minute, very lustrous, oblique prisms or plates, melting, when rapidly heated, at 230° , with evolution of gas—doubtless carbon monoxide, to judge from the analogy of the corresponding compound, $\text{C}_{34}\text{H}_{24}\text{O}_2$, obtained from anhydracetonebenzil (Japp and Burton, *Trans.*, 1887, 51, 426). It is sparingly soluble in solvents of low boiling point.

Analysis gave figures agreeing with those required for the formula $C_{36}H_{28}O_2$.

0.1321 gave 0.4240 CO_2 and 0.0734 H_2O . $C = 87.54$; $H = 6.18$.

$C_{36}H_{28}O_2$ requires $C = 87.82$; $H = 5.69$ per cent.

β -Methylanhydracetonebenzil is not altered by boiling with sulphuric acid of the foregoing strength, whilst a stronger acid chars it. Boiling it with acetic acid, and even heating with the acid in a sealed tube at 130° , gave only desylene-methyl ethyl ketone. Heating with formic acid, however, converts it into the compound $C_{36}H_{28}O_2$.

Four grams of β -methylanhydracetonebenzil and 16 grams of concentrated formic acid were heated in a sealed tube at 130° for 4 hours. The products were a pasty solid and a violet coloured liquid. The solid was dissolved in benzene, and light petroleum was added, which precipitated resinous matter. The filtrate yielded lustrous crystals of the compound $C_{36}H_{28}O_2$, which, after recrystallisation from acetic acid, melted at 230° with evolution of gas.

α - and β -Methylanhydracetonebenzil thus yield the same compound, $C_{36}H_{28}O_2$, by elimination of the elements of water. The reason for doubling the formula of this substance is given in the introduction.

Reduction of α - and β -Methylanhydracetonebenzil with Hydriodic Acid:

Formation of Methyl-diphenylcyclopentenone,
$$\begin{array}{c} C_6H_5 \cdot C \cdot CH(CH_3) \\ | \\ C_6H_5 \cdot C - CH_2 \end{array} > CO, \text{ and}$$

1-Methyl-2:3-diphenylcyclopentane,
$$\begin{array}{c} C_6H_5 \cdot CH \cdot CH(CH_3) \\ | \\ C_6H_5 \cdot CH - CH_2 \end{array} > CH_2. - \text{Ten}$$

grams of α -methylanhydracetonebenzil were boiled with excess of fuming hydriodic acid (sp. gr. 1.9) for 5 minutes. Excess of water was added, and the solid substance, separated by filtration, was dissolved in ether. The ethereal solution was shaken with dilute sulphurous acid, then with a solution of sodium carbonate, and dried with calcium chloride. On spontaneous evaporation, it gave crystals which, after repeated recrystallisation from light petroleum, were obtained in the form of faint yellow, oblique, flat prisms or plates melting constantly at $77-78^\circ$.

In another experiment, the residue which remained after expelling the ether was distilled under reduced pressure. The crude product passed over at about 200° under a pressure of 12 mm. This procedure considerably facilitated the purification of the substance, but was attended with loss. The compound was finally crystallised from light petroleum. It melted, as above, at $77-78^\circ$.

Analysis gave figures agreeing with those required for a *methyl-diphenylcyclopentenone*, $C_{18}H_{16}O$.

0.1936 gave 0.6179 CO_2 and 0.1146 H_2O . $C = 87.04$; $H = 6.58$.

0.1730 „ 0.5524 CO_2 „ 0.1013 H_2O . $C = 87.08$; $H = 6.50$.

$C_{18}H_{16}O$ requires $C = 87.10$; $H = 6.45$ per cent.

β -Methylanhydracetonebenzil was then reduced in precisely the same way with hydriodic acid. It yielded the same methyldiphenylcyclopentenone melting at 77—78°. A supersaturated solution of the compound thus prepared instantly crystallised on adding a little of the crystalline compound obtained from α -methylanhydracetonebenzil.

Methyldiphenylcyclopentenone forms a *phenylhydrazone*,

In preparing this compound, 1 gram of methyldiphenylcyclopentenone was heated with 1 gram of phenylhydrazine and about 6 c.c. of alcohol in a sealed tube for 5 hours at 100°. Addition of dilute acetic acid and, subsequently, of water, caused the separation of an oil; this was dissolved in warm alcohol. The solution deposited clusters of minute, yellow prisms melting with decomposition at from 145° to 152° according to the rate of heating. It decomposes on recrystallisation.

Analysis gave figures agreeing with those required for the foregoing *phenylhydrazone*.

0.1181 gave 8.5 c.c. moist nitrogen at 13.5° and 757 mm. N = 8.46.

$\text{C}_{24}\text{H}_{22}\text{N}_2$ requires N = 8.28 per cent.

In order to carry the reduction further than the formation of methyldiphenylcyclopentenone, and to obtain, if possible, the corresponding cyclopentane derivative, 10 grams of α -methylanhydracetonebenzil were boiled with 150 grams of hydriodic acid (sp. gr. 1.7) and 20 grams of red phosphorus for 5 hours. The product was worked up as described in the foregoing reduction experiments, removing iodine and then distilling under reduced pressure. A large fraction passed over between 160° and 200° under 20 mm. pressure; on standing, it solidified. On dissolving it in ether and adding methyl alcohol, tufts of colourless, slender needles separated; after recrystallising twice from the same solvents, they melted constantly at 62—63°. The substance was identical with the 1-methyl-2:3-diphenylcyclopentane obtained by Japp and Murray (Trans., 1897, 71, 153) by the reduction of α -anhydrobenzillævulic acid. A specimen prepared in the latter way at once started the crystallisation of a supersaturated solution of the present compound.

0.1791 gave 0.5990 CO_2 and 0.1380 H_2O . C = 91.20; H = 8.56.

$\text{C}_{18}\text{H}_{20}$ requires C = 91.52; H = 8.48 per cent.

Condensation of α -Methylanhydracetonebenzil with Benzil; Formation of α -Methylanhydracetonedibenzil, $\text{C}_{32}\text{H}_{26}\text{O}_4$.—The fact that anhydracetonebenzil interacts with benzil in presence of dilute alcoholic potassium hydroxide to form an aldol condensation compound, anhydr-

acetonedibenzil (Japp and Findlay, Trans., 1899, '75, 1025), led us to try whether α -methylanhydracetonebenzil would exhibit an analogous behaviour.

In our first experiment, we used the very dilute alcoholic potassium hydroxide which had proved efficacious in the previous condensations. The reaction took place ; but as the product proved to be a potassium salt, and as there was not sufficient potassium hydroxide present to form this salt with the whole of the other interacting substances, we repeated the experiment, using a stronger solution of the hydroxide, and obtained a much better result.

3.3 grams of α -methylanhydracetonebenzil and 2.5 grams of benzil were dissolved in 32 c.c. of alcoholic potassium hydroxide (2 grams of KOH to 100 c.c. of absolute alcohol). The solution was filtered into a small flask, which was corked up and the whole allowed to stand. (As the potassium salt cannot be recrystallised without decomposing it, it is necessary to obtain it pure at once.) After 4 days, there was a deposit of large, well-developed crystals ; these were separated, washed with cold alcohol, and air-dried by brief exposure on filter-paper. They effloresce on standing. The compound is a *potassium* salt of α -methylanhydracetonedibenzil, $C_{32}H_{26}O_4$, and has the complex formula $C_{32}H_{25}O_4K, C_{32}H_{26}O_4, 4C_2H_5 \cdot OH$. Like the sodium salt of ethyl anhydridibenzilacetoacetate (Japp and Lander, Trans., 1896, 69, 736), it is readily soluble in benzene and is totally decomposed by boiling with alcohol.

The potassium was determined in the ordinary way as sulphate ; the α -methylanhydracetonedibenzil by shaking a benzene solution of the salt with dilute hydrochloric acid, washing with water, and afterwards freeing from moisture and benzene, a process which could give only an approximate result ; and the alcohol of crystallisation by leaving the substance in a vacuum desiccator over sulphuric acid for 6 weeks, heating being inadmissible. The potassium determinations were made with different preparations.

0.5784 gave 0.0414 K_2SO_4 . $K = 3.21$.

0.7854 „ 0.0566 K_2SO_4 . $K = 3.23$.

2.0933 „ 1.737 $C_{32}H_{26}O_4$. $C_{32}H_{26}O_4 = 82.97$.

1.3482 lost, on drying, 0.2070. $C_2H_5 \cdot OH = 15.35$.

$C_{32}H_{25}O_4K, C_{32}H_{26}O_4, 4C_2H_6O$ requires $K = 3.33$; $C_{32}H_{26}O_4 = 81.02$;
 $C_2H_6O = 15.72$ per cent.

The *sodium* salt, which was not analysed, was obtained direct from benzil and methyl ethyl ketone. Ten grams of benzil and 6.8 grams of methyl ethyl ketone were added to 200 c.c. of absolute alcohol in which 4.4 grams of sodium had previously been dissolved. There was a slight rise of temperature and the benzil went into solution. After

standing overnight in a corked flask, the liquid had deposited a large quantity of needle-shaped crystals. The substance was worked up for α -methylanhydracetonedibenzil after standing for 3 days. It was identical with a sodium salt which we obtained by condensing α -methylanhydracetonebenzil with benzil by means of an alcoholic solution of sodium ethoxide.

In order to obtain free α -methylanhydracetonedibenzil, either the potassium or the sodium salt, prepared as already described, is washed with cold alcohol and dissolved in benzene in the cold. By adding glacial acetic acid until the solution has an acid reaction and then shaking with water, the alkali metal is removed. The α -methylanhydracetonedibenzil soon begins to separate in a crystalline form from the benzene solution; it is purified by recrystallisation from boiling alcohol. Two kinds of crystals are obtained: from the hot alcoholic solution, small, hard warty crystals melting at 194° ; from the cold solution, silky needles melting at 185° . The two forms may be readily changed one into the other, and neither contains solvent of crystallisation. The same two forms are deposited from a benzene solution.

On analysis, the substance gave figures agreeing with those required for the formula of α -methylanhydracetonedibenzil, $C_{32}H_{26}O_4$. Analysis I was made with the needles; analysis II with the warty crystals.

0.1488 gave 0.4396 CO_2 and 0.0748 H_2O . C = 80.57; H = 5.58.

0.1472 „ 0.4352 CO_2 „ 0.0750 H_2O . C = 80.63; H = 5.66.

$C_{32}H_{26}O_4$ requires C = 81.01; H = 5.48 per cent.

Like its analogue, ethyl anhydrodibenzilacetoacetate, it is difficult to burn.

As the composition of the potassium salt of α -methylanhydracetonedibenzil might be taken as pointing to a molecular weight twice as great as that represented by the formula $C_{32}H_{26}O_4$, an ebullioscopic determination of the molecular weight was made by the method already referred to, using alcohol (constant = 1560) as a solvent.

α -Methylanhydracetonedibenzil.

Substance.	Elevation.	Volume.	Mol. wt.
0.613	0.13°	17.5 c.c.	420
„	0.10	22.5	425
$C_{32}H_{26}O_4 = 474$.			

This result decides in favour of the lower molecular weight.

Ethylation of α -Methylanhydracetonedibenzil.—The fact that a hydrogen atom in ethyl anhydrodibenzilacetoacetate may be replaced by ethyl by boiling the compound with alcohol containing a few drops of

sulphuric acid (Japp and Lander, Trans., 1896, 69, 738) led us to try the same experiment with α -methyl-anhydracetonebenzil.

Five grams of α -methyl-anhydracetonebenzil, 100 c.c. of absolute alcohol, and 5 drops of concentrated sulphuric acid were boiled, using a reflux condenser. At first everything dissolved; but in a short time a separation of small crystals commenced, the amount of which gradually increased. After 3 hours, the operation was interrupted; the crystals were separated and washed with alcohol. They formed very sparingly soluble, colourless, short needles, melting at 250°.

Analysis showed that an ethyl derivative, $C_{32}H_{25}(OC_2H_5)_3$, had been formed.

0.1643 gave 0.4883 CO_2 and 0.0895 H_2O . C = 81.09; H = 6.05.

$C_{34}H_{30}O_4$ requires C = 81.27; H = 5.98 per cent.

Condensation of Benzil with other Ketones.

The condensations remaining to be described were all carried out by the methods already given for the preparation of α - and β -methyl-anhydracetonebenzil, the condensing agent being either alcoholic 0.5 per cent. potassium hydroxide (4 grams KOH to 1 litre of absolute alcohol) in the cold, or aqueous 33.3 per cent. potassium hydroxide at a temperature somewhat under 100° (see preparation of β -methyl-anhydracetonebenzil). Where two isomeric condensation compounds are formed, the former method generally gives, as already mentioned, the better yield of the compound of lower melting point. The separation of the two isomerides was effected by fractional crystallisation from alcohol, occasionally preceded by extraction of the more soluble isomeride with ether.

α -Desylene-ethyl Ethyl Ketone, $\begin{array}{c} C_6H_5 \cdot C : C(CH_3) \cdot CO \cdot C_2H_5 \\ | \\ C_6H_5 \cdot CO \end{array}$, and $\alpha\beta$ -Dimethyl-anhydracetonebenzil, $\begin{array}{c} C_6H_5 \cdot C \\ || \\ C_6H_5 \cdot C(OH) \cdot CH(CH_3) \end{array} > C(CH_3) > CO$.—In the experiment in which alcoholic potassium hydroxide was used, the proportions were: benzil, 10 grams; diethyl ketone, 7.5 grams; alcoholic potassium hydroxide (0.5 per cent.), 100 c.c., the whole being allowed to stand for a month. Crystals of $\alpha\beta$ -dimethyl-anhydracetonebenzil separated, but a great part remained in the mother liquor along with the more soluble α -desylene-ethyl ethyl ketone. The product was precipitated with water, and the crystalline precipitate resolved into its two constituents as already described in the precipitation of α -methyl-anhydracetonebenzil.

In the experiment with aqueous potassium hydroxide, the following proportions were used: benzil, 40 grams; diethyl ketone, 30 grams;

aqueous potassium hydroxide (33·3 per cent.), 30 c.c. Time of heating 24 hours. (For mode of heating and of working up, see preparation of β -methylanhydracetonebenzil.) The products were the same as in the previous experiment, but the proportion of $\alpha\beta$ -dimethylanhydracetonebenzil was greater. The yield of this compound was 27 grams.

$\alpha\beta$ -Dimethylanhydracetonebenzil crystallises from alcohol in colourless, rhomboidal plates or prisms, melting at 150°, as described by Japp and Burton (*loc. cit.*), by whom it was prepared and analysed.

α -Desylene-ethyl ethyl ketone is deposited from alcohol in large, oblique, four-sided prisms melting at 128°. Analysis showed that it was isomeric with the preceding compound.

0·1649 gave 0·4943 CO₂ and 0·0967 H₂O. C = 81·75 ; H = 6·52.

0·1670 „ 0·5012 CO₂ „ 0·0988 H₂O. C = 81·85 ; H = 6·57.

C₁₉H₁₈O₂ requires C = 82·01 ; H = 6·48 per cent.

α -Desylene-ethyl ethyl ketone is much more readily attacked by permanganate than $\alpha\beta$ -dimethylanhydracetonebenzil, indicating that it is structurally different from, not merely stereoisomeric with, the latter compound. It is probably fumaroid α -desylene-ethyl ethyl ketone, as the maleoid form might be expected to undergo internal aldol condensation to $\alpha\beta$ -dimethylanhydracetonebenzil under the influence of potassium hydroxide. This change, however, takes place under the influence of heat. A small quantity of α -desylene-ethyl ethyl ketone was heated in an atmosphere of carbon dioxide at 300—320° for 10 minutes. The fused mass, which had turned light brown, was dissolved in alcohol; on seeding the solution with a trace of $\alpha\beta$ -dimethylanhydracetonebenzil, it began to crystallise and deposited the characteristic rhomboidal plates of that substance, melting at 149° (m. p. 150°). The transformation occurs as follows :

The former compound thus corresponds with desylene-methyl ethyl ketone, which under the influence of heat is converted into β -methylanhydracetonebenzil (*v. supra*).

It may be noted that the transformation of α -desylene-ethyl ethyl ketone into $\alpha\beta$ -dimethylanhydracetonebenzil does not take place when the substance is heated in a vacuum, as under these circumstances it distils without change.

$\beta\beta$ -Dimethylanhydracetonebenzil, $\begin{array}{c} \text{C}_6\text{H}_5\cdot\text{C}\equiv\text{CH} \\ \text{C}_6\text{H}_5\cdot\text{C}(\text{OH})\cdot\text{C}(\text{CH}_3)_2 \end{array} \rangle \text{CO}$.—Only the method with alcoholic potassium hydroxide was employed. The

proportions were: benzil, 10 grams; methyl *isopropyl* ketone, 7.5 grams; alcoholic potassium hydroxide (0.5 per cent.), 125 c.c. The reaction was allowed to go on at the ordinary temperature. Crystals of the new compound separated within a day. After standing for three days, the product was worked up in the usual way. It crystallised from alcohol in clusters of prisms, with pyramidal ends, or in plates, melting at 181°. Only this one substance was formed in the reaction.

Analysis gave figures agreeing with the formula of $\beta\beta$ -dimethyl-anhydracetonebenzil.

0.1789 gave 0.5358 CO₂ and 0.1059 H₂O. C = 81.68; H = 6.58.

0.1326 „ 0.3968 CO₂ „ 0.0810 H₂O. C = 81.62; H = 6.80.

C₁₉H₁₈O₂ requires C = 82.01; H = 6.48 per cent.

That the compound is not an open-chain diketone follows from its high melting point.* That it is $\beta\beta$ -dimethylanhydracetonebenzil is shown by the product which it yields on oxidation. This will be described in a subsequent paper.

α -Ethylanhydracetonebenzil, $\begin{matrix} \text{C}_6\text{H}_5 \cdot \text{C} = \text{C}(\text{C}_2\text{H}_5) \\ \text{C}_6\text{H}_5 \cdot \text{C}(\text{OH}) \cdot \text{CH}_2 \end{matrix} > \text{CO}$, and β -Ethylanhydracetonebenzil, $\begin{matrix} \text{C}_6\text{H}_5 \cdot \text{C} = \text{CH} \\ \text{C}_6\text{H}_5 \cdot \text{C}(\text{OH}) \cdot \text{CH}(\text{C}_2\text{H}_5) \end{matrix} > \text{CO}$. — Forty grams of benzil, 30 grams of methyl *n*-propyl ketone, and 30 c.c. of aqueous 33.3 per cent. potassium hydroxide were heated for 16 hours in the way already described. The product, precipitated with water, washed with ether, and recrystallised from alcohol, formed minute needles melting at 156°, and was identical with the β -ethylanhydracetonebenzil prepared and analysed by Japp and Burton (*loc. cit.*). The ethereal extract gave a more soluble substance which crystallised from alcohol in large prisms, sometimes obliquely truncated, sometimes with pyramidal ends, melting at 114°. This proved to be α -ethylanhydracetonebenzil.

In a second experiment, 10 grams of benzil, 7.5 grams of methyl *n*-propyl ketone, and 125 c.c. of alcoholic potassium hydroxide (0.5 per cent.) were mixed and allowed to stand at the ordinary temperature for a month, although a shorter time would doubtless have sufficed. The solution had turned brown. The same products were obtained as in the previous experiment, but the yield of the α -compound was better.

Analysis of α -ethylanhydracetonebenzil (m. p. 114°) gave figures agreeing with those required for the formula C₁₉H₁₈O₂.

* Thus α -benzoyl- β -trimethacetylstyrene, $\begin{matrix} \text{C}_6\text{H}_5 \cdot \text{C} : \text{CH} \cdot \text{CO} \cdot \text{C}(\text{CH}_3)_3 \\ \text{C}_6\text{H}_5 \cdot \text{CO} \end{matrix}$, from benzil and methyl *tert.* butyl ketone (to be described in a later communication), melts as low as 115°.

0.1756 gave 0.5276 CO₂ and 0.1036 H₂O. C = 81.93 ; H = 6.55.

0.1644 „ 0.4934 CO₂ „ 0.0974 H₂O. C = 81.85 ; H = 6.58.

C₁₉H₁₈O₂ requires C = 82.01 ; H = 6.48 per cent.

Benzylidene-α-ethylanhydracetonebenzil,
$$\begin{array}{c} \text{C}_6\text{H}_5 \cdot \text{C} : \text{C}(\text{C}_2\text{H}_5) > \text{CO} \\ \text{C}_6\text{H}_5 \cdot \text{C}(\text{OH}) - \text{C} = \text{CH} \cdot \text{C}_6\text{H}_5 \end{array}$$

—One gram of α-ethylanhydracetonebenzil (m. p. 114°), 0.5 gram of benzaldehyde, and 12 c.c. of alcoholic potassium hydroxide (0.5 per cent.) were allowed to stand in a corked test-tube. As after 5 days nothing had separated, crystallisation was started by rubbing with a glass rod. The substance formed colourless needles. On heating, it showed signs of melting at 162—166°, but did not entirely melt until 178° was reached.

0.1748 gave 0.5437 CO₂ and 0.0961 H₂O. C = 84.84 ; H = 6.10.

C₂₆H₂₂O₂ requires C = 85.24 ; H = 6.01 per cent.

β-Ethylanhydracetonebenzil, treated in the same manner, showed no sign of interacting with benzaldehyde.

αβ-Trimethylanhydracetonebenzil,
$$\begin{array}{c} \text{C}_6\text{H}_5 \cdot \text{C} = \text{C}(\text{CH}_3) > \text{CO} \\ \text{C}_6\text{H}_5 \cdot \text{C}(\text{OH}) \cdot \text{C}(\text{CH}_3)_2 \end{array}$$
—The

condensation of benzil with ethyl isopropyl ketone did not take place readily. The best result, although far from a satisfactory one, was obtained by employing as a condensing agent a solution of sodium ethoxide in absolute alcohol.

Ten grams of benzil, 6 grams of ethyl isopropyl ketone, and 100 c.c. of absolute alcohol, in which 1.6 grams of sodium had previously been dissolved, were mixed and allowed to stand in a corked flask at the ordinary temperature for 2 months. A shorter time would probably have sufficed. The liquid turned dark, and there was a slight separation of crystals. Water was added, the precipitated substance was washed with ether to remove benzil, and the residue was recrystallised from alcohol. From hot solutions it was deposited in colourless, prismatic needles, by spontaneous evaporation in prisms, melting at 131°. The yield was less than a gram.

Analysis gave figures agreeing with the formula C₂₀H₂₀O₂.

0.1566 gave 0.4721 CO₂ and 0.0993 H₂O. C = 82.21 ; H = 7.04.

0.1721 „ 0.5171 CO₂ „ 0.1091 H₂O. C = 81.94 ; H = 7.04.

C₂₀H₂₀O₂ requires C = 82.19 ; H = 6.85 per cent.

The relatively low melting point might suggest that this is an open-chain compound. We therefore heated the substance for 10 minutes at 300—320° in an atmosphere of carbon dioxide, but, beyond volatilising and condensing again in slender needles, it underwent no change. We must therefore assume that it is, as above formulated,

αβ-trimethylanhydracetonebenzil, since all the open-chain compounds formed in these condensations are converted on heating into the isomeric closed chain derivatives. The question could be finally settled only by a study of the reactions of the compound, but the difficulty of obtaining the necessary ethyl *isopropyl* ketone, and the smallness of the yield of the condensation product, make this for the present impossible.

α-n-Propylanhydracetonebenzil, $\begin{array}{c} \text{C}_6\text{H}_5 \cdot \text{C} = \text{C}(\text{C}_3\text{H}_7) \\ | \\ \text{C}_6\text{H}_5 \cdot \text{C}(\text{OH}) \cdot \text{CH}_2 \end{array} > \text{CO}$, and *β-n-Propylanhydracetonebenzil*, $\begin{array}{c} \text{C}_6\text{H}_5 \cdot \text{C} = \text{CH} \\ | \\ \text{C}_6\text{H}_5 \cdot \text{C}(\text{OH}) \cdot \text{CH}(\text{C}_3\text{H}_7) \end{array} > \text{CO}$.—In the first experiment, 40 grams of benzil, 34 grams of methyl *n*-butyl ketone, and 30 c.c. of 33·3 per cent. aqueous potassium hydroxide were heated for 34 hours. The process was carried out as in the preparation of *β*-methylanhydracetonebenzil. In working up the product, the ethereal extract gave a substance which was deposited from ether in large, flat, obliquely truncated prisms, and from alcohol in six-sided plates, melting at 89°. This proved to be *α-n-propylanhydracetonebenzil*. The sparingly soluble residue, recrystallised from alcohol, was deposited in clusters of slender prisms melting at 152°. This was *β-n-propylanhydracetonebenzil*. It formed the chief product. The yield of purified *β*-compound was 12·5 grams.

In a second experiment, a mixture of 10 grams of benzil, 8·5 grams of methyl *n*-butyl ketone, and 125 c.c. of alcoholic potassium hydroxide (0·5 per cent.) was allowed to stand in a corked flask at the ordinary temperature for a month. The products were the same as in the former case, but the yield of *α-n-propylanhydracetonebenzil* was better.

Analysis of *α-n-propylanhydracetonebenzil* (m. p. 89°):

0·1783 gave 0·5372 CO₂ and 0·1077 H₂O. C = 82·19; H = 6·73.

0·1813 „ 0·5440 CO₂ „ 0·1162 H₂O. C = 81·83; H = 7·12.

C₂₀H₂₀O₂ requires C = 82·19; H = 6·85 per cent.

Analysis of *β-n-propylanhydracetonebenzil* (m. p. 152°):

0·1836 gave 0·5530 CO₂ and 0·1121 H₂O. C = 82·13; H = 6·78.

0·1850 „ 0·5570 CO₂ „ 0·1151 H₂O. C = 82·12; H = 6·90.

C₂₀H₂₀O₂ requires C = 82·19; H = 6·85 per cent.

Benzylidene-α-n-propylanhydracetonebenzil, $\begin{array}{c} \text{C}_6\text{H}_5 \cdot \text{C} : \text{C}(\text{C}_3\text{H}_7) \\ | \\ \text{C}_6\text{H}_5 \cdot \text{C}(\text{OH}) - \text{C} = \text{CH} \cdot \text{C}_6\text{H}_5 \end{array}$

—The condensation of *α-n-propylanhydracetonebenzil* with benzaldehyde was carried out as in the case of the other *α*-compounds, the reaction taking place in this case also in the cold. The benzylidene derivative was deposited from its hot alcoholic solution in clusters of small laminae melting at 166°.

0.1591 gave 0.4970 CO₂ and 0.0930 H₂O. C = 85.19 ; H = 6.49.

C₂₇H₂₄O₂ requires C = 85.26 ; H = 6.32 per cent.

β -n-Propylanhydracetonebenzil did not interact with benzaldehyde.

$\alpha\beta$ -Diethylanhydracetonebenzil, $\begin{array}{c} \text{C}_6\text{H}_5 \cdot \text{C} = \text{C}(\text{C}_2\text{H}_5) \\ \text{C}_6\text{H}_5 \cdot \text{C}(\text{OH}) \cdot \text{CH}(\text{C}_2\text{H}_5) \end{array} > \text{CO}$.—When benzil and dipropyl ketone were heated with aqueous potassium hydroxide, no condensation took place. The action of alcoholic potassium hydroxide in the cold, however, gave the desired result.

A mixture of 10 grams of benzil, 10 grams of dipropyl ketone, and 125 c.c. of alcoholic potassium hydroxide (0.5 per cent.) was allowed to stand in a corked flask at the ordinary temperature for a month. On pouring the product into water, an oil separated which speedily became crystalline. By recrystallisation from alcohol, only one product could be obtained: plates of rhombic outline, striated parallel to the shorter diagonal, melting at 113–114°. It was not changed by heating for 10 minutes at 300–320° in an atmosphere of carbon dioxide, thus showing that it is not an open-chain compound.

Analysis gave figures agreeing with those required for the formula of diethylanhydracetonebenzil.

0.1453 gave 0.4379 CO₂ and 0.0943 H₂O. C = 82.19 ; H = 7.21.

0.2047 „ 0.6180 CO₂ „ 0.1328 H₂O. C = 82.33 ; H = 7.20.

C₂₁H₂₂O₂ requires C = 82.35 ; H = 7.19 per cent.

α -n-Amylanhydracetonebenzil, $\begin{array}{c} \text{C}_6\text{H}_5 \cdot \text{C} = \text{C}(\text{C}_5\text{H}_{11}) \\ \text{C}_6\text{H}_5 \cdot \text{C}(\text{OH}) \cdot \text{CH}_2 \end{array} > \text{CO}$, and β -n-amylianhydracetonebenzil, $\begin{array}{c} \text{C}_6\text{H}_5 \cdot \text{C} = \text{CH} \\ \text{C}_6\text{H}_5 \cdot \text{C}(\text{OH}) \cdot \text{CH}(\text{C}_5\text{H}_{11}) \end{array} > \text{CO}$.—Forty grams of benzil, 44 grams of methyl n-hexyl ketone, and 30 c.c. of 33.3 per cent. aqueous potassium hydroxide were heated for 15 hours as described under the preparation of β -methylanhydracetonebenzil, the product being afterwards worked up in the usual way. Only β -amylianhydracetonebenzil—slender, silky needles melting at 150.5°, described and analysed by Japp and Burton—was obtained.

In a second experiment, a mixture of 10 grams of benzil, 11 grams of methyl n-hexyl ketone, and 125 c.c. of alcoholic potassium hydroxide (0.5 per cent.) was allowed to stand in a corked flask for a month. On pouring into water, the product which separated was partly crystalline, partly oily. The solid portion, after crystallisation from alcohol, yielded needles of β -amylianhydracetonebenzil melting at 150.5°. The oil, on long standing, also gave crystals—large, six-sided plates—which after recrystallising twice from light petroleum melted constantly at 57°, and proved to be the isomeric α -amylianhydracetonebenzil. The yield of the latter compound is fairly good.

Analysis of α -amylanhydracetonebenzil (m. p. 57°):

0.1763 gave 0.5338 CO_2 and 0.1210 H_2O . C = 82.56; H = 7.63.

0.1678 „ 0.5067 CO_2 „ 0.1142 H_2O . C = 82.35; H = 7.56.

$\text{C}_{22}\text{H}_{24}\text{O}_2$ requires C = 82.50; H = 7.50 per cent.

Benzylidene- α -amylanhydracetonebenzil,
$$\begin{array}{c} \text{C}_6\text{H}_5 \cdot \text{C} : \text{C}(\text{C}_5\text{H}_{11}) > \text{CO} \\ | \\ \text{C}_6\text{H}_5 \cdot \text{C}(\text{OH}) - \text{C} = \text{CH} \cdot \text{C}_6\text{H}_5 \end{array}$$

—This compound was prepared like the other benzylidene derivatives of α -compounds. It is deposited from its solution in boiling alcohol in colourless needles melting at 156° .

0.1595 gave 0.4985 CO_2 and 0.1011 H_2O . C = 85.21; H = 7.04.

$\text{C}_{29}\text{H}_{28}\text{O}_2$ requires C = 85.29; H = 6.86 per cent.

β -Amylanhydracetonebenzil does not interact with benzaldehyde.

One of us is at present engaged, conjointly with Mr. Arthur C. Michie, in studying the products of the oxidation of the various methyl homologues of anhydracetonebenzil.

The foregoing two 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 some years past been in part defrayed by various allotments from the Government Grant Fund of the Royal Society.

CHEMICAL DEPARTMENT,
UNIVERSITY OF ABERDEEN.