LXVII.—*Some Derivatives of Anhydracetonebenzil.*

By FRANCIS ROBERT JAPP, F.R.S., and JOSEPH KNOX, B.Sc., Carnegie Scholar in the University of Aberdeen.

THE condensations of benzil with saturated aliphatic ketones to form anhydracetonebenzil and its homologues have been studied in considerable detail by one of us in conjunction with various collaborators. It appeared of interest to ascertain what course the reaction would take in the case of an unsaturated ketone and to compare the product with that obtained from the corresponding saturated ketone. We selected for this purpose, as an unsaturated ketone, methyl *isobutenyl* ketone, $\text{CH}_3 \cdot \text{CO} \cdot \text{CH} : \text{C}(\text{CH}_3)_2$, and, as a saturated ketone, methyl *isobutyl* ketone.

Methyl *isobutenyl* ketone condenses with benzil under the influence of potassium hydroxide to form β -*isopropylideneanhydracetonebenzil*, $\text{C}_6\text{H}_5 \cdot \text{C} = \text{CH} \begin{array}{l} \diagup \text{CO} \\ \diagdown \end{array} \text{C}(\text{OH}) \cdot \text{C} = \text{C}(\text{CH}_3)_2$ (m. p. 205.5°), the reaction thus taking place exactly as in the case of the saturated ketones already studied, except that the presence of the bivalent *isopropylidene* group prevents the simultaneous formation of an isomeric α -compound. This condensation compound yields an *acetyl* derivative (m. p. 139 — 140° and 154 — 155° , dimorphous), the formation of which is rendered possible by the circumstance that the condensation compound has no hydrogen in the β -position, as otherwise derivatives of anhydracetonebenzil merely undergo dehydration under the influence of acetic anhydride. When reduced by brief boiling with hydriodic acid, β -*isopropylideneanhydracetonebenzil* yields *diphenylisopropylidenecyclopentenone*,

the usual change in the position of the double bonds, so as to form a stilbene group, occurring during the process (compare Japp and Murray, *Trans.*, 1897, **71**, 145; Japp and Meldrum, 1901, **79**, 1026).

Methyl *isobutyl* ketone and benzil, when condensed by means of potassium hydroxide, yield a mixture of α -*isopropylanhydracetonebenzil*, $\text{C}_6\text{H}_5 \cdot \text{C} = \text{C} \begin{array}{l} \diagup \text{CH}(\text{CH}_3)_2 \\ \diagdown \text{CO} \end{array} \text{C}(\text{OH}) \cdot \text{CH}_2$ (m. p. 142°), and β -*isopropylanhydr-*

acetonebenzil, $\text{C}_6\text{H}_5 \cdot \text{C} = \text{CH} \begin{array}{l} \diagup \text{CO} \\ \diagdown \end{array} \text{C}(\text{OH}) \cdot \text{CH} \begin{array}{l} \diagup \text{CO} \\ \diagdown \end{array} \text{CH}(\text{CH}_3)_2$ (m. p. 161.5°). The

former compound condenses with benzaldehyde, under the influence

of potassium hydroxide, to yield *benzylidene-α-isopropylbenzylideneacetone-benzil*,

$$\begin{array}{c} \text{C}_6\text{H}_5 \cdot \text{C} = \text{C} - \text{CH}(\text{CH}_3)_2 \\ | \quad \quad \quad \diagup \\ \text{C}_6\text{H}_5 \cdot \text{C}(\text{OH}) \cdot \text{C} = \text{CH} \cdot \text{C}_6\text{H}_5 \\ \quad \quad \quad \diagdown \\ \quad \quad \quad \text{CO} \end{array} \quad (\text{m. p. } 179^\circ).$$

We had originally contemplated carrying out the complete reduction of β -isopropylideneanhydrazetonebenzil, and of one of the isopropylanhydrazetonebenzils, with hydriodic acid and red phosphorus, so as to obtain, if possible, from both compounds the same hydrocarbon—diphenylisopropylcyclopentane—and thus to prove more conclusively the relation existing between them; but the separation of the two isopropylanhydrazetonebenzils was so difficult that we were compelled to relinquish our intention. Moreover, a preliminary experiment showed that the reduction of β -isopropylideneacetonebenzil beyond the cyclopentenone stage did not yield a very satisfactory product.

At the end of the present paper we describe improved methods for the preparation of anhydrazetonebenzil and β -methylanhydrazetonebenzil.

EXPERIMENTAL.

I. Condensation of Benzil with Methyl isoButenyl Ketone.

Twenty grams of benzil, 15 grams of methyl isobutenyl ketone ("mesityl oxide"), and 15 c.c. of an aqueous solution of potassium hydroxide of 33.3 per cent. strength were introduced into a conical flask fitted with a condensing tube, and the whole was heated for 4 hours on a thin metal plate over a water-bath,* the flask being shaken from time to time. The product, which was very dark-coloured, was poured into warm water, when a black, oily substance separated; this was washed with water and then left until it became semi-solid, after which it was spread on a porous tile. The substance, freed from adhering oil, was recrystallised several times from hot benzene and was thus obtained in slender, yellow needles melting at 205.5°. The yield was 7 grams.

0.1632 gave 0.4929 CO₂ and 0.0911 H₂O. C=82.37; H=6.20.

$\text{C}_{20}\text{H}_{18}\text{O}_2$ requires C = 82.76 ; H = 6.20 per cent.

The same substance was obtained by condensing benzil with methyl *isobutenyl* ketone in the cold by means of a 0.5 per cent. solution of potassium hydroxide in absolute alcohol; but the yield was even poorer than in the preceding case.

* This arrangement gives a temperature of from 60° to 70°, provided that no steam is allowed to condense between the plate and the flask.

[View Article Online](#)

A portion of the substance was heated for 10 minutes at 310° (diphenylamine vapour) in an atmosphere of carbon dioxide. It resolidified on cooling and, after recrystallisation from benzene, was found to consist of unchanged substance (m. p. 205.5°). A sublimate which had formed in the upper part of the tube gave the same melting point.

The foregoing result shows that the condensation product is a closed-chain compound, inasmuch as all open-chain compounds formed by the condensation of benzil with ketones are changed on heating, yielding closed-chain compounds. Thus desylene-methyl ethyl ketone is in this way transformed into β -methylanhydracetonebenzil (Japp and Meldrum, *Trans.*, 1901, **79**, 1031).

An attempt to synthesise β -isopropylideneanhydracetonebenzil by condensing acetone with anhydracetonebenzil under the influence of alcoholic potassium hydroxide—a process which, if benzaldehyde be substituted for acetone, readily yields benzylideneanhydracetonebenzil—led to no result.

Acetyl Derivative.—One gram of β -isopropylideneanhydracetonebenzil and 10 grams of acetic anhydride were mixed, and 1 drop of concentrated sulphuric acid was added. (If this proportion of acid is exceeded, a very impure product is obtained.) This addition caused the solid substance to dissolve, yielding a dark brown solution. After three days the mixture was poured into excess of water, and the yellow, flocculent precipitate which gradually separated, was purified by recrystallisation, first from alcohol, afterwards from benzene with addition of light petroleum (sp. gr. 0.71 — 0.72), and finally from light petroleum alone. It was thus obtained in slender, colourless needles. It melts at 139 — 140° and, if kept a little above this temperature, resolidifies, finally melting at 154 — 155° . This phenomenon is doubtless due to dimorphism, and not to chemical change, inasmuch as a specimen which had been melted as above, then allowed to cool, and recrystallised from light petroleum, again gave the same two melting points.

Analysis showed that a *monacetyl* derivative had been formed.

0.1566 gave 0.4570 CO_2 and 0.0857 H_2O . $\text{C} = 79.58$; $\text{H} = 6.08$.

$\text{C}_{22}\text{H}_{20}\text{O}_3$ requires $\text{C} = 79.51$; $\text{H} = 6.02$ per cent.

β -isoPropylideneanhydracetonebenzil is not acetylated by boiling it for 4 hours with a mixture of acetic anhydride and anhydrous sodium acetate.

Reduction of β -isoPropylideneanhydracetonebenzil with Hydriodic Acid: Formation of Diphenylisopropylidenecyclopentenone,

—Two grams of β -isopropylideneanhydrazetonebenzil (m. p. 205.5°) were boiled for 8 minutes with 40 grams of fuming hydriodic acid (sp. gr. 1.96). Water was added, the organic substance was dissolved in ether, and the ethereal solution was shaken successively with aqueous sulphurous acid, sodium carbonate solution, and water. During the latter part of the process, a crystalline substance separated from the ether; it was filtered off and recrystallised from benzene, from which it was deposited in thick prisms melting constantly at 171° . The dried ethereal filtrate, on evaporation, yielded a further quantity of this substance, which was purified in the same way. Yield: 0.6 gram.

0.1448 gave 0.4647 CO_2 and 0.0863 H_2O . C = 87.52; H = 6.62.

$\text{C}_{20}\text{H}_{18}\text{O}$ requires C = 87.59; H = 6.57 per cent.

II. Condensation of Benzil with Methyl isoButyl Ketone.

—Forty grams of finely powdered benzil, 28 grams of methyl isobutyl ketone, and 400 c.c. of a 0.5 per cent. solution of potassium hydroxide in absolute alcohol were shaken in a corked flask until the benzil had dissolved, after which the mixture was left for 12 days. The solution was then diluted with water until it became turbid, and allowed to crystallise. The crystalline deposit, which weighed 51 grams, proved to be a mixture of two substances—one of them dimorphous—which were very difficult to separate. Fractional crystallisation proved unavailing, although nearly all the ordinary organic solvents were tried. Finally we had to resort to the tedious process of picking out the different kinds of crystals. The crystalline product was dissolved in benzene, and somewhat less than an equal volume of light petroleum (sp. gr. 0.71–0.72) was added. The solution deposited colourless, six-sided prisms, white, silky needles, and flat, yellow prisms. The three kinds of crystals were separated mechanically.

The six-sided prisms were recrystallised repeatedly from benzene with the addition of light petroleum until they showed the constant melting point of 142° . The white, silky needles also melted at 142° , and a mixture of these with the six-sided prisms gave no depression of melting point. When either the six-sided prisms or the silky needles are crystallised from benzene with addition of light petroleum, a mixture of prisms and needles is obtained in each case. When a

[View Article Online](#)

mixture of the prisms and needles is allowed to stand with a mixture of benzene and light petroleum insufficient to dissolve them, the needles gradually disappear, being transformed into the prisms. The substance melting at 142° is thus dimorphous, the six-sided prisms being the stable form at the ordinary temperature. This substance is *α-isopropylanhydracetonebenzil*, as is shown by its yielding a benzylidene derivative (*v. infra*).

0.2151 gave 0.6477 CO_2 and 0.1339 H_2O . $\text{C} = 82.12$; $\text{H} = 6.91$.

$\text{C}_{20}\text{H}_{20}\text{O}_2$ requires $\text{C} = 82.19$; $\text{H} = 6.84$ per cent.

This compound (m. p. 142°) was recovered unchanged after being heated for 5 minutes at 330° in an atmosphere of carbon dioxide. This result indicates that the substance is a closed-chain condensation product, as formulated.

The flat, yellow prisms were recrystallised from light petroleum (sp. gr. 0.71–0.72). The compound, which is *β-isopropylanhydracetonebenzil*, was thus obtained in flat, colourless needles, melting constantly at 161.5° . *β*-Monalkylanhydracetonebenzils melt higher than the corresponding *α*-derivatives.

0.1563 gave 0.4711 CO_2 and 0.0980 H_2O . $\text{C} = 82.20$; $\text{H} = 6.96$.

$\text{C}_{20}\text{H}_{20}\text{O}_2$ requires $\text{C} = 82.19$; $\text{H} = 6.84$ per cent.

The quantity of this compound was too small, and its separation too difficult, to allow of our investigating it further.

Benzylidene-α-isopropylanhydracetonebenzil,

—One gram of *α-isopropylanhydracetonebenzil* (m. p. 142°) and 0.4 gram of benzaldehyde were shaken with a 1 per cent. solution of potassium hydroxide in absolute alcohol until the whole dissolved. After 12 days the liquid was diluted with half its volume of water. The crystals which were deposited weighed 1 gram. They were twice recrystallised from benzene, with the addition of light petroleum, and were thus obtained in the form of four-sided prisms, with oblique or pointed ends. They melted constantly at 179° .

0.1623 gave 0.5062 CO_2 and 0.0948 H_2O . $\text{C} = 85.06$; $\text{H} = 6.49$.

$\text{C}_{27}\text{H}_{24}\text{O}_2$ requires $\text{C} = 85.26$; $\text{H} = 6.31$ per cent.

III. Improved Methods of Preparing Anhydracetonebenzil and *β*-Methylanhydracetonebenzil.

Anhydracetonebenzil.—Acetonebenzil, $\begin{array}{c} \text{C}_6\text{H}_5 \cdot \text{CO} \\ | \\ \text{C}_6\text{H}_5 \cdot \text{C}(\text{OH}) \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{CH}_3 \end{array}$, and

anhydracetonebenzil, $\text{C}_6\text{H}_5 \cdot \text{C} \begin{array}{l} \text{---} \text{CH} \\ \text{---} \text{C}(\text{OH}) \cdot \text{CH}_2 \end{array} > \text{CO}$, were first prepared by Japp and Miller (*Trans.*, 1885, 47, 21 and 27), who, however, assigned to the latter compound a constitution different from the foregoing and termed it "dehydracetonebenzil." The former compound was obtained by the action of a small quantity of aqueous potassium hydroxide on a mixture of benzil and acetone, the latter was formed from the same substances when an excess of potassium hydroxide was used.

Both of these substances were subsequently prepared on several occasions ; but the yields varied in an unaccountable manner. It was evident that much depended on the character of the acetone. Japp and Miller found that a specimen of acetone purified merely by fractional distillation could not be used in the preparation of acetonebenzil. They say : "The employment of an acetone purified by means of the bisulphite compound is in this reaction *indispensable*—not merely for obtaining a good yield of the compound, but in order to obtain any of the compound at all." Japp and Klingemann, however (*Trans.*, 1890, 57, 673, footnote), found that acetone could be prepared so pure as not to give the reaction, but that the same acetone readily condensed with benzil under the influence of a little aqueous potassium hydroxide to form acetonebenzil, if two or three drops of alcohol were previously added to it.*

We have now had a similar experience in the preparation of anhydracetonebenzil. Working according to the directions given by Japp and Lander (*Trans.*, 1897, 71, 130), who improved upon the original process, and using Kahlbaum's "acetone from the bisulphite compound," we obtained hardly any anhydracetonebenzil, the greater part of the benzil being recovered unchanged. This was the more surprising, as Japp and Lander, in preparing the very large quantities of anhydracetonebenzil which they required for their study of the oxidation of this compound, had not merely employed this method, but had used acetone of the same quality, also obtained from Kahlbaum, although of a different preparation.

Mindful of Japp and Klingemann's experience with acetonebenzil, we repeated the process, adding, however, a few drops of alcohol to the mixture. The effect was such that we obtained a yield even better than that recorded by Japp and Lander.

As this slight modification may thus mean all the difference between failure and success in the preparation of anhydracetonebenzil, and as it renders the course of the reaction independent of minute differences

* I pointed out (*loc. cit.*) that the "pure" acetone prepared by Dr. Miller and myself may have contained traces of alcohol derived from the commercial ether which was used in washing the bisulphite compound.—F. R. J.

[View Article Online](#)

in the quality of the acetone employed, we will describe the method in detail.

Two hundred grams of finely-powdered benzil, 125 grams of pure acetone (Kahlbaum's acetone "from the bisulphite compound"), 1 c.c. of alcohol, and 2 c.c. of an aqueous solution of potassium hydroxide of 33·3 per cent. strength were shaken in a corked flask until the whole of the benzil had dissolved. The liquid became slightly warm during the process, owing to the formation of the aldol condensation compound, acetonebenzil. Fifty more c.c. of the aqueous potassium hydroxide were then added, and the mixture was warmed for half an hour on the water-bath, during which time it was frequently shaken. The whole was then poured into hot water, and the organic substance, which solidified on cooling, was ground in a mortar, washed, first with hot water and then with a little ether to remove dark-coloured impurities, and finally recrystallised from hot benzene. In this way we obtained, from the foregoing quantities, 165 grams of anhydracetonebenzil (m. p. 147° *), without working up the mother liquors, whereas Japp and Lander, who did not add alcohol to the mixture, obtained only 150 grams in all.

It must be borne in mind that although the addition of a small quantity of alcohol thus facilitates the occurrence of the reaction, the condensation of benzil and acetone to form anhydracetonebenzil cannot be effected by means of an alcoholic solution of potassium hydroxide, since under these circumstances the anhydracetonebenzil formed in the first instance condenses with a second molecule of benzil to form anhydracetonedibenzil.

β-Methylanhydracetonebenzil.—Of the two monomethyl homologues of anhydracetonebenzil—*α*-methylanhydracetonebenzil,

and *β*-methylanhydracetonebenzil, $\begin{array}{c} \text{C}_6\text{H}_5 \cdot \text{C} = \text{CH} \\ \text{C}_6\text{H}_5 \cdot \text{C}(\text{OH}) \cdot \text{CH}(\text{CH}_3) \end{array} > \text{CO}$ — the

α-compound is readily obtained, together with only a mere trace of the *β*-compound, by the protracted action of a 0·5 per cent. solution of potassium hydroxide in absolute alcohol on a mixture of benzil and methyl ethyl ketone in the cold; whereas, when *aqueous* potassium hydroxide of 33·3 per cent. strength is used, and the mixture is heated,

* This is the melting point of *yellow* anhydracetonebenzil as ordinarily obtained, the yellow colour being due to the presence of a trace of benzyldeneanhydracetonebenzil which cannot be removed except by a wasteful process of partial oxidation of the substance. The pure compound is colourless and melts at 149°, but the yellow substance is sufficiently pure for all ordinary purposes (compare Japp and Miller Trans., 1885, 47, 27; Japp and Findlay, 1899, 75, 1018 and 1019)

[View Article Online](#)

the proportion of β -compound formed is increased, remaining, however, below that of the α -compound which is simultaneously produced, so that the yield of β -compound still leaves much to be desired (Japp and Meldrum, Trans., 1901, 79, 1028).

We now find that by substituting aqueous sodium hydroxide for potassium hydroxide in the latter reaction the yield of β -compound is very appreciably improved.

Eighty grams of benzil, 50 grams of methyl ethyl ketone, 0.5 c.c. of alcohol, and 60 c.c. of a solution of sodium hydroxide prepared by dissolving the *commercial** hydroxide in twice its weight of water, were introduced into a conical flask fitted with a condensing tube, and the whole was heated for $3\frac{1}{2}$ hours on a thin metal plate over a water-bath, the flask being shaken from time to time. The product was poured into hot water, and the solidified substance was ground, washed with water, freed from dark-coloured impurities by treatment with a little ether, and dissolved in boiling alcohol. The solution, on cooling, deposited 24 grams of practically pure β -methylanhydracetonebenzil. The mother liquor contained α -methylanhydracetonebenzil and α -desylenemethyl ethyl ketone, together with a small quantity of β -methylanhydracetonebenzil; these could be separated by fractional crystallisation from alcohol. It is to be noted that desylenemethyl ethyl ketone can be converted quantitatively into β -methylanhydracetonebenzil by heating it for a short time at 330° (Japp and Meldrum, Trans., 1901, 79, 1031).

A second experiment conducted in the same way also gave 24 grams of the β -compound, whereas in a previous experiment in which the same quantities of benzil and methyl ethyl ketone were heated with aqueous *potassium* hydroxide of 33.3 per cent. strength only 19 grams were obtained.

CHEMICAL DEPARTMENT,
UNIVERSITY OF ABERDEEN.

* In one experiment, in which we employed *pure* sodium hydroxide, the solution made up in the above proportions proved to be too strong, and considerable resinification of the organic substances occurred.