

## ON $\alpha$ -OXYBENZYLIDENE ACETOPHENONE.

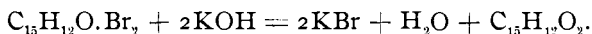
BY F. J. POND, H. J. YORK, AND B. L. MOORE.

Received August 2, 1901.

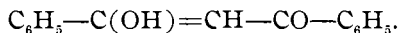
It has been shown in a previous paper<sup>1</sup> that when benzylidene acetophenone dibromide,  $C_{15}H_{12}O.Br_2$ , is treated with sodium alcoholate, it is readily converted into a compound,  $C_{15}H_{12}O_2$ , which is identical in all respects with the substance long known as *dibenzoyl methane*. The latter compound was first prepared by Baeyer and Perkin<sup>2</sup> by boiling dibenzoyl acetic acid ester with water during several hours; it was subsequently studied by Claisen,<sup>3</sup> who obtained it by the action of metallic sodium or sodium ethylate upon a mixture of acetophenone and benzoic acid ester. This compound was represented as a  $\beta$ -diketone, having the formula



Almost simultaneous with the publication of the above-mentioned paper in this Journal, J. Wislicenus<sup>4</sup> published an article "On the Isomeric Forms of Dibenzoyl Methane." According to Wislicenus, two molecular proportions of potassium or sodium hydroxide dissolved in alcohol react with benzylidene acetophenone dibromide in accordance with the equation



The product,  $C_{15}H_{12}O_2$ , consists of a mixture of two isomeric compounds of the same melting temperature, one of which is identical with Baeyer and Perkin's, and Claisen's dibenzoyl methane; this compound is unsaturated, and Wislicenus designates it as  *$\alpha$ -oxybenzylidene acetophenone*,



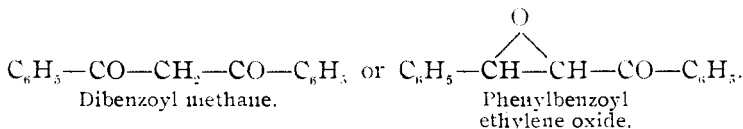
The second isomeric compound,  $C_{15}H_{12}O_2$ , is saturated, and may prove to be the true dibenzoyl methane or, possibly, a substance having a molecule constituted like ethylene oxide,

<sup>1</sup> Pond, Maxwell, and Norman: This Journal, **21**, 955.

<sup>2</sup> Baeyer and Perkin: *Ber. d. chem. Ges.*, **16**, 2134; *J. Chem. Soc.* (London), **47**, 250.

<sup>3</sup> L. Claisen: *Ber. d. chem. Ges.*, **20**, 655; *Ann. Chem.* (Liebig), **291**, 52.

<sup>4</sup> J. Wislicenus: *Ann. Chem.* (Liebig), **308**, 219.



Since in our previous experiments on the action of sodium methylate upon benzylidene acetophenone dibromide only one compound was obtained, it seemed desirable to continue this investigation and to compare this compound with those described by Wislicenus.

The results of this investigation indicate that sodium methylate reacts in a manner somewhat different from that of alcoholic potash; and that the substance formed in this reaction, which was called dibenzoyl methane in the previous paper and was proved to be identical with the compound described under this name by Claisen, should be termed  $\alpha$ -oxybenzylidene acetophenone.

#### EXPERIMENTAL.

*Benzylidene Acetophenone*,  $\text{C}_6\text{H}_5-\text{CH}::\text{CH}-\text{CO}-\text{C}_6\text{H}_5$ .—This compound is most conveniently prepared according to the method of Claisen<sup>1</sup> by the action of a small quantity of a 20 per cent. solution of sodium methylate upon a mixture of the molecular proportions of acetophenone and benzaldehyde. Claisen purified this product by repeated crystallizations from petroleum ether; this method is slow and rather unsatisfactory, since the compound is not easily soluble in this solvent, and it requires a number of recrystallizations to remove oily impurities. It was found that it could be purified readily and quickly by crystallizing from alcohol; it separates in large crystals, melting at  $57^\circ$  to  $58^\circ$ .

$\alpha$ - and  $\beta$ -*Benzylidene Acetophenone Dibromides*,  $\text{C}_{13}\text{H}_{12}\text{O}.\text{Br}_2$ .—By the addition of one molecular proportion of bromine to a solution of benzylidene acetophenone in chloroform, Claisen<sup>2</sup> obtained a dibromide, melting at  $156^\circ$  to  $157^\circ$ , which is difficultly soluble in cold alcohol. J. Wislicenus<sup>3</sup> also mentions that benzylidene acetophenone is almost completely precipitated from its chloroform solution, on the addition of one molecule of bromine, as a very difficultly soluble dibromide,



<sup>1</sup> Claisen and Claparède: *Ber. d. chem. Ges.*, 14, 2463.

<sup>2</sup> Claisen: *Ber. d. chem. Ges.*, 14, 2463.

<sup>3</sup> J. Wislicenus: *Ann. Chem. (Liebig)*, 308, 223.

after one crystallization from boiling alcohol, it is obtained in snow-white, pure crystals, melting at  $156.5^{\circ}$  to  $157.5^{\circ}$ . Hitherto, no mention appears to have been made of an isomeric dibromide and it is quite probable that it has been overlooked, although it is formed in small quantity whenever benzylidene acetophenone unites with bromine.

If a solution of 25 grams of benzylidene acetophenone in 125 cc. of ether be treated gradually with 20.8 grams (2 atoms) of bromine, and, after standing for a few minutes, the almost colorless solution is filtered by means of the pump from the thick, white precipitate, a considerable quantity of the new isomeric dibromide is obtained from the filtrate. The difficultly soluble compound is washed well with ether, crystallized from alcohol, and obtained as the pure white dibromide, melting at  $157.5^{\circ}$ . The analysis gave :

I. 0.1632 gram gave 0.1660 gram silver bromide.

II. 0.1510 gram gave 0.1530 gram silver bromide.

	Calculated for $C_{15}H_{12}O.Br_2$ .	I.	Found.	II.
Bromine.....	43.48	43.29		43.12

It is sparingly soluble in alcohol and ether, and will be termed  $\alpha$ -benzylidene acetophenone dibromide in order to distinguish it from the lower melting, more soluble isomeric or  $\beta$ -dibromide.

The ethereal solution and wash-ether are treated with a small quantity of sulphurous acid in order to remove any slight excess of bromine, then washed well with water, and the ether allowed to evaporate ; the new  $\beta$ -dibromide is obtained from the residue. The latter is extracted with a limited quantity of boiling alcohol in order to separate a very small quantity of the comparatively insoluble  $\alpha$ -compound, and, after evaporation of the alcohol, the  $\beta$ -dibromide is repeatedly crystallized from boiling alcohol. It separates in aggregates of small, fine needles, which melt at  $108^{\circ}$  to  $109^{\circ}$ . We usually obtained 3 to 4 grams of the  $\beta$ -dibromide by this method. It was analyzed with the following results :

I. 0.2002 gram gave 0.3570 gram carbon dioxide and 0.0635 gram water.

II. 0.3400 gram gave 0.3471 gram silver bromide.

III. 0.3436 gram gave 0.3509 gram silver bromide.

	Calculated for $C_{15}H_{12}O.Br_2$ .	I.	Found.	III.
Carbon.....	48.91	48.63	....	....
Hydrogen.....	3.26	3.47	....	....
Bromine.....	43.48	....	43.44	43.45

It dissolves at  $30^{\circ}$  in 106 parts of ethyl alcohol,  $96.7^{\circ}$  Tr., while the  $\alpha$ -dibromide, at the same temperature, requires 610 parts of alcohol. It is also more readily soluble in ether than the  $\alpha$ -compound. On raising the temperature about  $20^{\circ}$  above its melting-point and then allowing to solidify, it again melts at  $108.5^{\circ}$ .

The crystalline forms of the two dibromides are quite distinct, the  $\alpha$ - separating in short prisms, while the  $\beta$ -derivative crystallizes in fine needles.

It has also been observed that on brominating smaller quantities (about 5 grams) of benzylidene acetophenone at a time, and by adding the bromine rapidly, without cooling, a larger yield of the  $\beta$ -compound results. Although we usually employed ether as the solvent for the benzylidene acetophenone, nevertheless the formation of the isomeric bromide takes place when chloroform, carbon tetrachloride, or carbon disulphide is used. In all cases, however, the sparingly soluble  $\alpha$ -dibromide (m. p.  $157.5^{\circ}$ ) constitutes the chief product.

When the  $\alpha$ -dibromide is heated under pressure with ethyl or methyl alcohol, hydrobromic acid is eliminated, but as yet no definite crystalline derivatives have been obtained which correspond with those so readily formed by merely boiling anisylidene acetophenone dibromide with ethyl or methyl alcohol.<sup>1</sup> On heating 20 grams of the  $\alpha$ -dibromide with 100 cc. of methyl alcohol for three hours at  $120^{\circ}$ , a substance resulted which melted at  $117^{\circ}$  to  $119^{\circ}$ ; this product has not, however, proved to be a definite chemical compound, and will be further studied. The change appears to take place between  $110^{\circ}$  and  $125^{\circ}$ ; on heating the  $\alpha$ -dibromide with methyl alcohol at a temperature below  $110^{\circ}$ , the unchanged compound is recovered; above  $125^{\circ}$  the substance suffers decomposition.

*The Action of Two Molecules of Sodium Methylate upon the  $\alpha$ -Dibromide.*—To a solution of sodium methylate (8 grams of sodium in 200 cc. of methyl alcohol), 50 grams of  $\alpha$ -benzylidene acetophenone dibromide were added, and boiled for thirty minutes in a reflux apparatus. Three hundred and fifty cc. of water were then introduced and the liquid rendered neutral or very slightly acid with dilute acetic acid. The oil which separated was extracted with ether, washed well with water, and dried over

<sup>1</sup> Pond and Shoffstall: This Journal, **22**, 668 and 670.

anhydrous sodium sulphate. After evaporation of the ether, some of the oil was distilled under diminished pressure; it boiled at  $206^{\circ}$  to  $210^{\circ}$  under 12 mm. pressure, yielding a mobile, yellow oil, which had a slight odor of decomposition; it did not become solid after standing in a closed vessel for several months. Analysis of this distillate gave the following results:

I. 0.2243 gram gave 0.6360 gram carbon dioxide and 0.1345 gram water.

II. 0.1978 gram gave 0.5609 gram carbon dioxide and 0.1226 gram water.

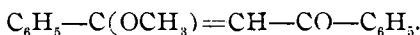
Analysis of oil prepared as above described, but which was not distilled, gave:

III. 0.1761 gram gave 0.5059 gram carbon dioxide and 0.0975 gram water.

IV. 0.1448 gram gave 0.4173 gram carbon dioxide and 0.0792 gram water.

	Calculated for $C_{10}H_{14}O_2$ .	I.	II.	Found.	III.	IV.
Carbon . . . . .	80.64	77.33	77.34	78.36	78.63	
Hydrogen . . . . .	5.88	6.66	6.93	6.15	6.07	

It was thought that the action of the sodium methylate consisted in removing one molecule of hydrogen bromide from the  $\alpha$ -dibromide and replacing the remaining bromine atom with the methoxyl group, thus giving rise to the unsaturated *methyl ether of  $\alpha$ -oxybenzylidene acetophenone*,



It has been impossible, however, to obtain analyses of this oil which would agree more closely with the calculated values for the methyl ether, although many analyses have been made on various samples of the oil purified by different methods. It is clear, therefore, that the oil is not a pure ether, but in the light of subsequent experiments it seems rather probable that the oil consists of a mixture of the ether with some compound, possibly derived from it. The oil reacts as an unsaturated compound; its alcoholic solution at once decolorizes a permanganate solution; when dissolved in ether it absorbs bromine, but on evaporation of the solution hydrobromic acid is eliminated and a non-characteristic oil is obtained.

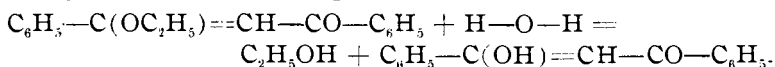
If the oil is the methyl ether suspected, or consists to some extent of this compound, it would be expected that dilute acids would convert it by hydrolysis into  $\alpha$ -oxybenzylidene acetophenone. The following experiment indicates that this reaction actually does take place.

Some of the oil was placed into a flask and treated with fairly

concentrated hydrochloric acid ; in a very short time (one or two minutes) the entire quantity of oil was converted into the solid  $\alpha$ -oxy-compound (m. p.  $77^{\circ}$  to  $78^{\circ}$ ). This was repeated with different mineral acids of varying strength, also with acetic acid, and it was found that the oil was in each case converted into the solid compound, although with very dilute acids the action requires a longer time for its completion. On standing in an open dish in the laboratory the change is more gradual, but in a month's time the oil is almost completely converted into the solid  $\alpha$ -oxy-compound. If this oil be placed in a closed vessel, it may be kept unchanged for a long time. We have retained a specimen in a desiccator, over fused calcium chloride, for nine months without the least trace of a solid being formed ; when, however, a drop of it was brought in contact with dilute acid it was almost immediately changed into the solid compound.

When  $\alpha$ -benzylidene acetophenone dibromide was treated with 2 molecules of sodium *ethylate* in the same manner as with the methylate, a reddish colored oil resulted ; this oil was analyzed with results similar to those above mentioned. It has properties similar to those of the oil resulting by the methylate treatment, decomposes on distillation at atmospheric pressure, distills with slight decomposition under reduced pressure, and is converted into  $\alpha$ -oxybenzylidene acetophenone by contact with acids. It may contain the unsaturated *ethyl ether of  $\alpha$ -oxybenzylidene acetophenone*, as indicated by the following experiment.

Eight grams of the red oil, previously well washed with water, dried over calcium chloride, and maintained for some time at  $110^{\circ}$ , were treated with 32 cc. of hydrochloric acid (1 : 1) ; in a short time the oil was converted into a solid, with a slight evolution of heat. The solid was filtered off, crystallized from alcohol and recognized as  $\alpha$ -oxybenzylidene acetophenone, melting at  $77^{\circ}$  ; the presence of ethyl alcohol in the filtrate was readily and distinctly determined by means of the iodoform reaction. This change is doubtless to be represented by the formula



That is, the oil undoubtedly contains the ethyl ether which is hydrolyzed by dilute acids, yielding ethyl alcohol and the  $\alpha$ -oxy-compound.

*$\alpha$ -Oxybenzylidene Acetophenone*,  $C_6H_5-C(OH)=CH-CO-C_6H_5$ .—This compound is readily obtained in good yield by treating the oil which results from the action of 2 molecules of sodium alcoholate upon  $\alpha$ -benzylidene acetophenone dibromide with fairly concentrated hydrochloric acid. It is also easily formed by boiling the oil with acetic acid and then precipitating with ice-water. The crude product melts at  $76^\circ$  to  $77^\circ$ , and frequently has a slight yellow to reddish tinge. It is best purified by conversion into its copper salt and decomposition of the latter by dilute hydrochloric acid. It crystallizes well from methyl or ethyl alcohol; when the alcoholic solution is fairly concentrated, the crystals are obtained in the form of long needles, but from dilute solutions it separates in large plates or tablets; the latter form of crystals are also obtained from ether. Both modifications melt sharply at  $77^\circ$  to  $78^\circ$ , thus confirming J. Wislicenus<sup>1</sup> observations regarding the melting-point of the so-called dibenzoyl methane. Analysis gave the results:

- I. 0.2895 gram gave 0.8530 gram carbon dioxide and 0.1380 gram water.  
 II. 0.2997 gram gave 0.8880 gram carbon dioxide and 0.1500 gram water.

	Calculated for $C_{15}H_{12}O_2$ .	I.	Found.	II.
Carbon.....	80.36	80.35		80.80
Hydrogen.....	5.35	5.29		5.56

It may be noted here that this compound agrees completely in properties with the substance described by J. Wislicenus as  $\alpha$ -oxybenzylidene acetophenone (formerly called dibenzoyl methane), but in no case have we obtained a trace of the isomeric compound observed by Wislicenus. It reacts readily with an alcoholic solution of copper acetate, forming the *copper salt*,<sup>2</sup>  $C_{30}H_{22}O_4Cu$ ; this is insoluble in alcohol and ether, and only sparingly soluble in chloroform and benzene. It melts at  $294^\circ$  to  $301^\circ$  with decomposition.

The *iron salt* is precipitated on the addition of molecular quantities of ferric chloride and sodium acetate to an alcoholic solution of the  $\alpha$ -oxy-compound; it is obtained in the form of a brick-red powder.

When a solution of  $\alpha$ -oxybenzylidene acetophenone is boiled with 2 molecular proportions of hydroxylamine hydrochloride,

<sup>1</sup> J. Wislicenus: *Ann. Chem. (Liebig)*, **308**, 228.

<sup>2</sup> J. Wislicenus: *Ibid.*, **308**, 231.

$\alpha\gamma$ -diphenyl isoxazole,<sup>1</sup>  $C_{15}H_{11}NO$ , is formed ; it separates from alcohol in brilliant, white leaflets, and melts at  $141^{\circ}$  to  $142^{\circ}$ . The same compound results on treating the alcoholic solution of  $\alpha$ -benzylidene acetophenone dibromide with aqueous solutions of hydroxylamine hydrochloride and potassium hydroxide ; it crystallizes from alcohol and melts at  $141.5^{\circ}$ .

On the addition of one molecule of bromine to a solution of the  $\alpha$ -oxy-compound in chloroform, hydrogen bromide is given off and *mono*-bromdibenzoyl methane,<sup>2</sup>  $C_{15}H_{11}BrO_2$ , is produced. It separates from alcohol in fine, white crystals, melting at  $91.5^{\circ}$  to  $92.5^{\circ}$ .

On boiling  $\beta$ -benzylidene acetophenone dibromide with sodium alcoholate it was thought that a compound isomeric with  $\alpha$ -oxybenzylidene acetophenone, and possibly identical with Wislicenus' second compound, might result ; this does not, however, appear to be the case. Ten grams of the  $\beta$ -dibromide were treated as usual with 2 molecules of sodium methylate ; after adding water and carefully neutralizing with dilute acetic acid, the resultant oil was extracted with ether, dried with anhydrous sodium sulphate, and the ether evaporated. The oil was then boiled for a short time with acetic acid and poured into ice-water ; it solidified rapidly and crystallized from alcohol in long needles, melting at  $77^{\circ}$  to  $78^{\circ}$  ; it separated from ether in plates of the same melting-point. In alcoholic solution it gave an immediate deep purple coloration with ferric chloride, and was quantitatively converted into the green copper salt by the addition of an alcoholic solution of copper acetate. It is therefore identical with the above described  $\alpha$ -oxybenzylidene acetophenone.

In the future we propose to investigate more thoroughly the new  $\beta$ -dibromide, and to ascertain whether it is possible to convert this compound into an isomeric modification of benzylidene acetophenone.

<sup>1</sup> J. Wislicenus : *Ann. Chem.* (Liebig), **308**, 248 ; see also Goldschmidt : *Ber. d. chem. Ges.*, **28**, 2540.

<sup>2</sup> Neufville and Pechmann : *Ber. d. chem. Ges.*, **23**, 5377 ; J. Wislicenus : *Ann. Chem.* (Liebig), **308**, 247.