Summary

1. It has been proved that the experimental results of Smith, Boord, Adams and Pease are erroneous on the following grounds.

(a) Past experience has shown that bodies of the type examined show only continuous absorption from 2350 Å. to 2000 Å.

(b) The absorption of two out of the four substances concerned has been measured and no evidence of a benzene-like structure such as is claimed has been found.

(c) It has been pointed out that benzene may have been present as an impurity either in the material or apparatus in amounts sufficient to explain the results reported by these authors.

2. Their theoretical deductions have also been shown to be unconvincing.

3. It has been pointed out that in this type of work absolute purity of the compounds examined and cleanliness of the apparatus used are essential.

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[CONTRIBUTION FROM THE PEARSON MEMORIAL LABORATORY OF TUFTS COLLEGE]

THE SYNTHESIS OF ALPHA,BETA-DIACYLSTYRENES AND THEIR REACTION WITH HYDROGEN BROMIDE

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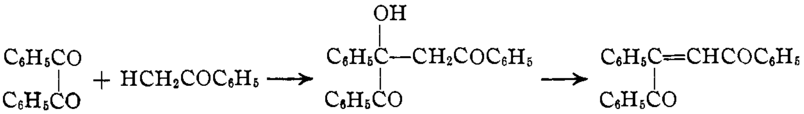
Japp and his co-workers[1] found that in the presence of alcoholic potassium hydroxide, benzil reacts with acetophenone and forms first an addition product (I), and finally an unsaturated diketone (II), which they called anhydracetophenone benzil or α,β-dibenzoylstyrene.[2]



$$\begin{matrix} C_6H_5CO \\ | \\ C_6H_5CO \end{matrix} + HCH_2COC_6H_5 \longrightarrow \begin{matrix} OH \\ | \\ C_6H_5C{-}CH_2COC_6H_5 \\ | \\ C_6H_5CO \end{matrix} \longrightarrow \begin{matrix} C_6H_5C{=}CHCOC_6H_5 \\ | \\ C_6H_5CO \end{matrix}$$

I II

We have found that many other dibenzoylstyrenes can be made in this manner, but that the reaction is not general. It was possible to substitute for the acetophenone used by Japp a number of other methyl ketones which had alkyl groups or chlorine atoms in the nucleus, while with other closely related methyl ketones the reaction failed. Thus, di-

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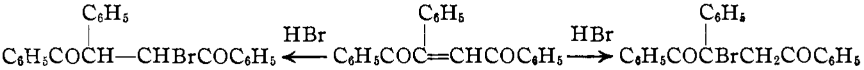
[1] Japp and co-workers, *J. Chem. Soc.*, (a) **47**, 35 (1885); (b) **51**, 430 (1887); (c) **53**, 184 (1888); (d) **57**, 662 (1890); (e) **71**, 1138 (1897); *Ber.*, (f) **18**, 187 (1885); (g) **21**, 2933 (1888).

[2] It might better be called phenyldibenzoylethylene, but the naming of compounds substituted in one benzoyl group seems clearer if they are considered as derivatives of styrene.

acylstyrenes were made successfully by condensing benzil with $CH_3COC_6H_5$, $CH_3COC_6H_4CH_3(4)$, $CH_3COC_6H_3(CH_3)_2(3,4)$, $CH_3COC_6H_4OCH_3(4)$, $CH_3COC_6H_3(OCH_3)_2(3,4)$, $CH_3COC_6H_4Cl(4)$, $CH_3COC_6H_4Br(4)$ and $CH_3COC_6H_3(CH_3)(3)Cl(4)$. The reaction was tried unsuccessfully with $CH_3COC_6H_3(CH_3)_2(2,4)$, $CH_3COC_6H_3(CH_3)_2(2,5)$, $CH_3COC_6H_3(CH_3)(2)(i\text{-}C_3H_7)(5)$, $CH_3COC_6H_3Cl(2)(CH_3)(5)$ and $CH_3COC_6H_2(CH_3)_3(2,4,5)$, the benzil being recovered unchanged. A comparison of the results shows that the reaction fails whenever there is a substituent in the *ortho* position of the acetophenone. This is a peculiar effect of hindrance for which at present there appears to be no adequate explanation. It seems to imply that some kind of addition reaction or complex formation involving the carbonyl group of the methyl ketone must precede condensation.

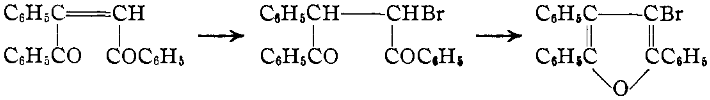
The styrene derivatives which are obtained in this manner have an ethylenic linkage that is conjugated with two carbonyl groups. They could therefore add substances of the type HX in two ways. Thus, hydrogen bromide could combine with dibenzoylstyrene to form either A or B.



$$C_6H_5CO\overset{C_6H_5}{C}H\text{—}CHBrCOC_6H_5 \xleftarrow{HBr} C_6H_5CO\overset{C_6H_5}{C}\text{=}CHCOC_6H_5 \xrightarrow{HBr} C_6H_5CO\overset{C_6H_5}{C}BrCH_2COC_6H_5$$

A II B

In a series of papers dealing with addition reactions of α,β unsaturated ketones, Kohler[3] has shown that while 1:4 addition is prevented if there are two substituent groups in the beta position to the carbonyl group, it takes place readily with compounds having alpha substituents, but at a slower rate than when both positions are unsubstituted. If this relation holds for substances containing conjugated systems of the type in the dibenzoylstyrenes, then the addition product with hydrogen bromide should be A. This is a 1:4 diketone with hydrogen atoms alpha to each carbonyl group; it would, therefore, be expected to lose water easily and form a bromofurane.



II A III

We have found that when α,β-dibenzoylstyrene in chloroform or acetic acid solution is treated with hydrogen bromide, the bromofurane (III) separates in nearly the calculated yield. The presence of the third phenyl group appears to favor ring closure because both the saturated bromoketone and the bromofurane can be isolated when hydrogen bromide is added to a chloroform solution of dibenzoylethylene, the corresponding unsubstituted diketone.[4] We have also found that this transformation

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[3] Kohler, *Am. Chem. J.*, 1905–1911.

[4] Paal and Schulze, *Ber.*, **35**, 172 (1902). Pratt, *Dissertation*, Harvard University, **1927**.

of an unsaturated diketone into a bromofurane is quite general, as it took place with all but one of the diacylstyrene derivatives.

Experimental Part

A. Condensation of Benzil and Substituted Acetophenones.—The general directions are as follows. One-twentieth mole of benzil and one-twentieth mole of the ketone are warmed with 5 cc. of methyl alcohol until dissolved. A solution of 0.2 g. of sodium in 25 cc. of methyl alcohol is added, the mixture kept near the boiling point for a few minutes and then allowed to stand overnight. The product is filtered off, washed with dil. alcohol until free from alkali, and recrystallized by dissolving in the smallest possible amount of boiling chloroform and adding an equal volume of methyl alcohol. Glacial acetic acid may also be used for recrystallization. The diketones form small, light yellow prisms almost insoluble in the alcohols and ether, sparingly soluble in acetone, but easily soluble in hot chloroform, acetic anhydride, and acetic acid. Yields, 80–85%.

TABLE I

DERIVATIVES OF α,β-DIBENZOYLSTYRENE

No.	Ketone used[a] (acetophenone derivation)	M. p., °C.	Formula	Analyses Calcd., % C	Analyses Calcd., % H	Analyses Found, % C	Analyses Found, % H
II	Acetophenone	129					
IV	4-Methyl-	158	$C_{23}H_{18}O_2$	84.7	5.5	84.3	5.6
V	3,4-Dimethyl-[b]	190	$C_{24}H_{20}O_2$	84.7	5.9	84.5	5.8
VI	4-Methoxy-[c]	177[d]	$C_{23}H_{18}O_3$	80.7	5.3	80.9	5.2
VII	3,4-Dimethoxy-[c]	177[d]	$C_{24}H_{20}O_4$	77.4	5.4	77.1	5.2
VIII	4-Chloro-	183	$C_{22}H_{15}O_2Cl$	76.1	4.3	76.2	4.4
IX	4-Chloro-3-methyl-[e]	189	$C_{23}H_{17}O_2Cl$	76.3	4.7	76.3	4.6
X	4-Bromo-	208	$C_{22}H_{17}O_3Br$	64.5	4.1	64.6	4.5

[a] Prepared by the method of Adams and Noller, THIS JOURNAL, **46**, 1889 (1924).

[b] This unsaturated compound may be isolated in a 15% yield when the commercial mixed dimethylacetophenones are condensed with benzil; it is interesting to note that it separates without traces of any other isomers.

[c] Insol. in chloroform, and recrystallized from acetic acid, in which it is slightly soluble.

[d] Mixed melting point, 148–150°.

[e] For the preparation of this ketone and the 2-chloro-5-methyl isomer we are indebted to Mr. M. P. Bridgess.

The condensation is not brought about by the use of pyridine, piperidine, nor a trace of sodium methylate. Two g. of potassium hydroxide in 3 cc. of water and 25 cc. of methyl alcohol may be used, however, but the product is not of as good quality.

B. The Formation of the 4-Bromofuranes.—The unsaturated diketones readily form bromofuranes when solutions in glacial acetic acid or chloroform are treated with hydrogen bromide. The procedure is to dissolve 5 g. in 20 cc. of warm acetic acid and saturate the solution by passing through a rapid current of dry hydrogen bromide gas. In some instances the bromofuranes separate almost immediately but always after standing overnight. They all form a white, bulky precipitate of needles that felt together on filtration, and show practically the same properties except melting point. Purification is best effected by dissolving in the minimum amount of hot chloroform and adding an equal volume of alcohol. The yields are practically quantitative.

TABLE II

2,3,5-TRIPHENYL-4-BROMOFURANE AND HOMOLOGS

No.	Group in position 5	M. p., °C.	Formula	Analyses Calcd., % C	H	Found, % C	H
III	Phenyl[a]	129	$C_{22}H_{15}OBr$				
XI	4-Methyl-	134	$C_{23}H_{17}OBr$	71.0	4.4	70.8	4.5
XII	3,4-Dimethyl-	137	$C_{24}H_{19}OBr$	71.5	4.7	71.6	4.9
XIII	4-Methoxy-	151	$C_{23}H_{17}O_2Br$	68.1	4.2	67.9	4.2
XIV	4-Chloro-[b]	127	$C_{22}H_{14}OClBr$	64.4	3.4	64.1	3.2
XV	4-Chloro-3-methyl-	135	$C_{23}H_{16}OClBr$	65.4	3.8	65.4	3.9
XVI	4-Bromo-[b]	157	$C_{22}H_{14}OBr_2$	58.1	3.1	58.0	3.1

[a] This bromofurane has been prepared once previously by the action of heat on two stereoisomeric γ-bromo-γ-nitro ketones. E. P. Kohler, private communication.

[b] Dissolved in 50 cc. of acetic acid.

The bromofuranes are very sparingly soluble in the alcohols, but dissolve readily in warm ether, chloroform, benzene and glacial acetic acid. They do not reduce permanganate in acetone solution nor decolorize bromine. The bromine atom is not affected by prolonged boiling with alkalies; bromide ion cannot be detected after twenty hours of heating with alcoholic potash. It does not react with magnesium to form a Grignard reagent, a result not unexpected, since the bromine atom is di-*ortho* substituted.

This work has been assisted by a generous grant from the Cyrus M. Warren Fund of the American Academy of Arts and Sciences.

Summary

1. Benzil readily condenses with acetophenones substituted in the *meta* or *para* positions in the presence of an equivalent of sodium methylate to form derivatives of phenyldibenzoylethylene.

2. These substances react with hydrogen bromide in such a way that the product formed is a 4-bromofurane. The bromine atom in the latter substance is inactive.

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