activity. It was also observed that the thymyl derivative exhibited a greater germicidal activity against *Bacillus typhosus* than *Staphylococcus aureus*.

The pharmacological results were somewhat more noteworthy. The cat and rabbit were used as test animals. It was found that the ureides were eliminated in the urine and that they were non-toxic in any concentration in which they might appear in the blood. It is significant to note that these ureides, when introduced into the femoral vein of the cat in the form of their sodium salts, produced no effect on respiration or blood pressure as recorded by the carotid blood pressure, provided that the rate of administration was not too rapid.

All of these ureides showed a very low toxicity. Five hundred milligrams, given in suspension by a stomach tube to rabbits, produced no toxic effect, no purgation, no diuresis, no hypnosis, no anesthesia and no excitement. The phenolsulfonphthalein test was not affected.

Summary

Twenty-eight compounds have been prepared. They are of the general nature RSR$_2$, where R may be NO$_2$, NH$_2$, or NH$_2$CONH, and R$_2$ may be the phenyl, resorcyl, *m*-cresyl or thymyl radical. Some bromo derivatives and acetates have been made. The diazotized amines were coupled with certain intermediates to form azo dyes. Twenty-four of these compounds have not been previously described in the literature.

The ureide derivatives have been tested bacteriologically. Only the thymyl ureide has been found to have any germicidal activity.

The ureides have also been tested pharmacologically, and it was shown that they were promptly excreted by way of the urinary tract.

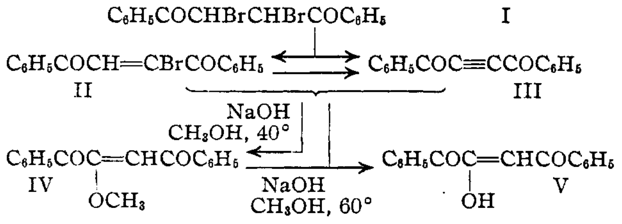
BALTIMORE, MD. RECEIVED JUNE 4, 1934

[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA, NO. 134]

The Tautomerism of 1,4-Diphenylbutane-1,2,4-trione Enol

BY ROBERT E. LUTZ, F. N. WILDER AND C. I. PARRISH

The 1,2,4-triketones and their enols are of interest because they combine the properties of α-, β- and γ-diketones, and because in the enolic forms they react like unsaturated 1,4-diketones. 1,2-Di-(trimethylbenzoyl)-ethenol has been prepared in both keto and enol forms by the action of alcoholic sodium acetate on di-(trimethylbenzoyl)-dibromoethane,[1a] but the analogous reactions in the dibenzoyl series[1] give materials which are not easily characterized and which have proved to be complex mixtures of secondary products. Diphenylbutanetrione, $C_6H_5COCOCH_2COC_6H_5$, has not as yet been isolated in the keto form, but the enol, which we regard as dibenzoylethenol V, may be prepared in good yield by the action of alcoholic sodium hydroxide on dibenzoyldibromoethane I, dibenzoylacetylene III, or dibenzoylmethoxyethylene IV.



The chain of reactions involved in this synthesis, starting with dibenzoyldibromoethane, possibly proceeds as indicated in the above diagram; in any case, each compound cited has been isolated under controlled conditions and reacts further as indicated to give the enol.[2] Sodium methylate, or sodium hydroxide in 92% methanol, reacts in the cold with dibenzoyldibromoethane or with dibenzoylacetylene to give dibenzoylmethoxyethylene IV even when an excess of alkali is used; however, the methyl ether is hydrolyzed to the enol by the excess of alkali when the mixtures are heated at 60° for five minutes. It is noteworthy that, even in the 92% methanolic solution, sodium methylate appears to be the primary reactant rather than sodium hydroxide, since the elements of methanol and not of water are involved and the enol arises from hydrolysis of the first formed methyl ether. Other enol ethers, including the phenyl, are hydrolyzed to the enol

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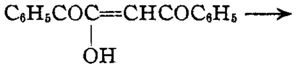
(1) (a) Lutz, THIS JOURNAL, **48**, 2905 (1926); (b) Conant and Lutz, *ibid.*, **47**, 881 (1925).

(2) For the isolation of dibenzoylbromoethylene and dibenzoylacetylene, see Ref. 1.

with equal ease in contrast with the di-(trimethylbenzoyl) analogs which are much less reactive in this sense.[3]

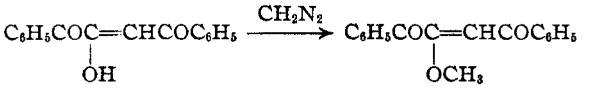
Hydrolysis of dibenzoylethenol with boiling aqueous barium hydroxide cleaves the molecule, yielding phenylglyoxylic acid and acetophenone.



$$C_6H_5CO\underset{\underset{OH}{|}}{C}=CHCOC_6H_5 \longrightarrow C_6H_5COCOOH + CH_3COC_6H_5$$

The enol exists in two easily interconvertible isomeric forms, one yellow and the other colorless. The yellow isomer is converted into the colorless by the action of direct or diffused light (on the solid material). When either form is dissolved in alcohol an equilibrium mixture results, which contains considerable amounts of the yellow form since the solutions are yellow; however, the less soluble colorless isomer is obtained exclusively on crystallization (a process which takes place slowly, due doubtless to a low rate of isomerization at the temperature involved). In chloroform solution the yellow isomer predominates as is shown by the fact that rapid evaporation in the cold or crystallization by means of added petroleum ether gives this form exclusively (the colorless isomer being practically insoluble in petroleum ether). The molten material consists largely of the yellow enol which is obtained exclusively on rapid chilling and crystallization. The yellow form can be recrystallized from petroleum ether, but when heated with the higher boiling ligroin it slowly undergoes rearrangement into the colorless enol which is almost completely insoluble in the alkane solvents. Slow distillation in a vacuum oven gives exclusively the yellow isomer as a crystalline deposit. From these facts it would appear that the yellow isomer is the more stable of the two; it is by far the more soluble in the alkane solvents, and is the more volatile; it is therefore a typically chelated enol in contrast with the colorless isomer which appears to be non-chelated.

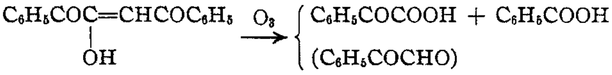
Both of the enols react vigorously with an ether solution of diazomethane at −10° giving in each case 50–65% yields of the same dibenzoylmethoxyethylene the structure of which is established by reduction to dibenzoylmethoxyethane and diphenylmethoxyfuran.[4]



$$C_6H_5CO\underset{\underset{OH}{|}}{C}=CHCOC_6H_5 \xrightarrow{CH_2N_2} C_6H_5CO\underset{\underset{OCH_3}{|}}{C}=CHCOC_6H_5$$

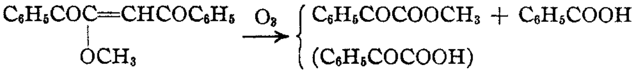
These results show that dibenzoylethenol actually exists in solution under these conditions as one of the components of an equilibrium mixture. The colorless non-chelated enol, which should be the more acidic and the more reactive toward diazomethane, very probably is the component which is reacting and has the dibenzoylethenol structure V.

Ozonization of the enol in chloroform solution, involving presumably the yellow form which is the stable one in this solvent, gives nearly one equivalent each of phenylglyoxylic and benzoic acids and only a small amount of the expected phenylglyoxal.



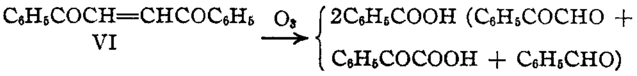
$$C_6H_5CO\underset{\underset{OH}{|}}{C}=CHCOC_6H_5 \xrightarrow{O_3} \begin{cases} C_6H_5COCOOH + C_6H_5COOH \\ (C_6H_5COCHO) \end{cases}$$

The phenylglyoxylic acid must be formed directly by fission of the dibenzoylethenol structure, and the benzoic acid by the breakdown of the other fission product, phenylglyoxal, a conclusion which is supported by the results of ozonization of certain other related compounds under the same conditions. Dibenzoylmethoxyethylene IV, in which the positions of the double bond and the methoxyl group are known, reacts in exactly the same sense as the enol to give nearly one equivalent each of benzoic acid and phenylglyoxylic acid methyl ester, and only a trace of phenylglyoxylic acid.



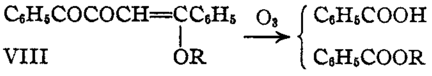
$$C_6H_5CO\underset{\underset{OCH_3}{|}}{C}=CHCOC_6H_5 \xrightarrow{O_3} \begin{cases} C_6H_5COCOOCH_3 + C_6H_5COOH \\ (C_6H_5COCOOH) \end{cases}$$

Dibenzoylethylene VI gives nearly two equivalents of benzoic acid and only very small amounts of phenylglyoxylic acid and phenylglyoxal (however, when the ozonization was carried out in 94% acetic acid the yield of phenylglyoxal was considerably higher, and some benzaldehyde was apparently formed also).



$$\underset{VI}{C_6H_5COCH=CHCOC_6H_5} \xrightarrow{O_3} \begin{cases} 2C_6H_5COOH\ (C_6H_5COCHO + \\ C_6H_5COCOOH + C_6H_5CHO) \end{cases}$$

The methyl and ethyl ethers (VIII) of the tautomeric enol $C_6H_5COCOCH{=}C(OH)C_6H_5$ (VII), give largely benzoic acid and the alkyl benzoate without the formation of significant amounts of phenylglyoxylic acid



$$\underset{VIII}{C_6H_5COCOCH}=\underset{\underset{OR}{|}}{C}C_6H_5 \xrightarrow{O_3} \begin{cases} C_6H_5COOH \\ C_6H_5COOR \end{cases}$$

It is therefore very unlikely that the hypothetical benzoylglyoxal, $C_6H_5COCOCHO$ (from fission of

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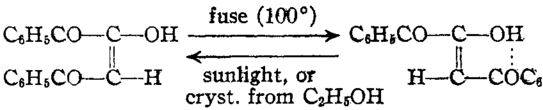
[3] Lutz, THIS JOURNAL, **56**, 1590 (1934).

[4] Lutz, *ibid.*, **51**, 3008 (1929).

both VII and VIII), is the source of the nearly theoretical yield of phenylglyoxylic acid in ozonization of the enol.

These results show that the enol undergoing ozonization (undoubtedly the yellow form) has the dibenzoylethenol structure V and is analogous to di-(trimethylbenzoyl)-ethenol.[3]

We are convinced from the various facts considered in the foregoing discussion that the two solid enols are stereoisomers of dibenzoylethenol (V), although the evidence is not conclusive. On the basis of stability and color relationships and the transformation of the yellow isomer into the colorless by the action of sunlight, the colorless enol has been tentatively assigned the *cis* configuration IX and the yellow enol the *trans* (X) (di-(trimethylbenzoyl)-ethenol, which is *trans*, is yellow[3]).

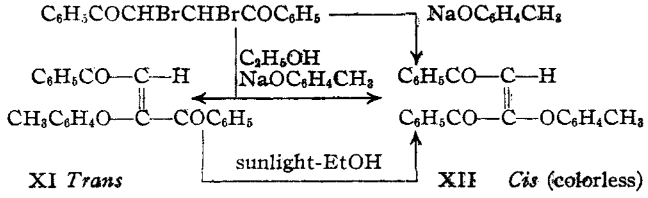


$$\begin{array}{c}C_6H_5CO{-}C{-}OH\\ \|\\ C_6H_5CO{-}C{-}H\end{array} \underset{\text{sunlight, or cryst. from } C_2H_5OH}{\overset{\text{fuse }(100°)}{\rightleftarrows}} \begin{array}{c}C_6H_5CO{-}C{-}OH\\ \|\\ H{-}C{-}COC_6H_5\end{array}$$

Cis IX (colorless) *Trans* X (yellow)

The physical properties of the two enols, namely, the relative solubilities and the higher volatility of the yellow form, are in agreement with those which would be expected on the basis of the above configurations, since chelation between the enolic hydroxyl and the β-carbonyl is conceivable only in the *trans* compound X in which these groups lie close together in space.

Only one of the two theoretically possible methyl ethers of dibenzoylethenol is known. Attempts to prepare the stereoisomer failed, including isomerization by means of alcoholates, a method used successfully with the di-(trimethylbenzoyl)-ethenol ethers.[3] Only in the case of the 3-methylphenoxy ethers[4] are two stereoisomers known; the yellow form (in the fused state or in solution) is *trans* (XI) since it undergoes rearrangement in the sunlight in ethanol into the colorless stereoisomer (which on this basis must be *cis*, XII). The preparation and structure of these two stereoisomers are therefore to be represented as follows

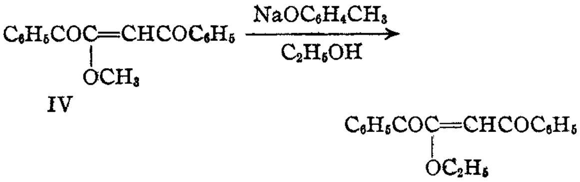


$$C_6H_5COCHBrCHBrCOC_6H_5 \xrightarrow{\text{Ether, } NaOC_6H_4CH_3} \text{XII}; \quad \begin{array}{c}C_6H_5CO{-}C{-}H\\ \|\\ CH_3C_6H_4O{-}C{-}COC_6H_5\end{array} \underset{\text{sunlight-EtOH}}{\overset{C_2H_5OH,\ NaOC_6H_4CH_3}{\rightleftarrows}} \begin{array}{c}C_6H_5CO{-}C{-}H\\ \|\\ C_6H_5CO{-}C{-}OC_6H_4CH_3\end{array}$$

XI *Trans* XII *Cis* (colorless)

The dibenzoylethenol methyl, ethyl and phenyl ethers, and also the colorless 3-methylphenyl ether XII when the preparation is carried out under very mild conditions, are the primary products of the action of sodium alcoholates or phenolates on dibenzoyldibromoethane. With respect to the mode of preparation they are analogous to the *cis* ethers of di-(trimethylbenzoyl)-ethenol;[3] furthermore, they are colorless and are stable toward sunlight in contrast with the stereoisomeric 3-methylphenyl ether XI and the *trans* di-(trimethylbenzoyl)-ethenol methyl and ethyl ethers.[3] The methyl ether IV, on the basis of these analogies (and also the probable correspondence in structure and configuration with the non-chelated *cis* dibenzoylethenol), appears to be of the *cis* configuration.

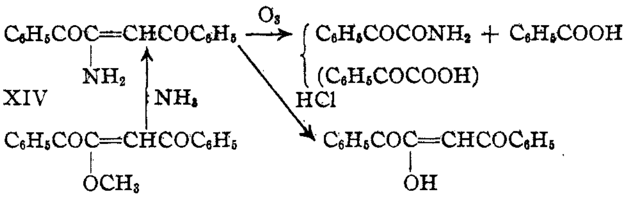
Alcoholysis of the methyl ether IV was accomplished by heating with ethanol and sodium 3-methylphenoxide and results in the replacement of methyl by ethyl giving dibenzoylethoxyethylene XIII (known[1b]), a reaction analogous to that between di-(trimethylbenzoyl)-ethenol ethers and alcoholates;[3] the yield however is only 15%.



$$C_6H_5CO\underset{\underset{OCH_3}{|}}{C}{=}CHCOC_6H_5 \xrightarrow[C_2H_5OH]{NaOC_6H_4CH_3} C_6H_5CO\underset{\underset{OC_2H_5}{|}}{C}{=}CHCOC_6H_5$$

IV XIII

Ammonolysis of dibenzoylmethoxyethylene gives dibenzoylamminoethylene (the ammono analog of the enol). This compound is obtained also by the action of ammonia on dibenzoyldibromoethane or on dibenzoylacetylene.[1] The structure XIV was established by ozonization,



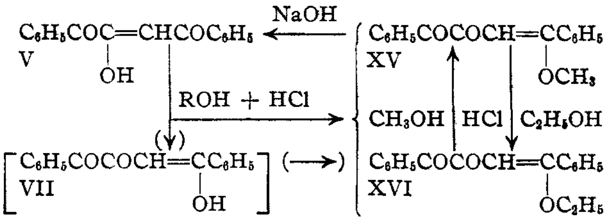
$$C_6H_5CO\underset{\underset{NH_2}{|}}{C}{=}CHCOC_6H_5 \xrightarrow{O_3} \left\{\begin{array}{l}C_6H_5COCONH_2 + C_6H_5COOH\\ (C_6H_5COCOOH)\end{array}\right.$$

$$C_6H_5CO\underset{\underset{OCH_3}{|}}{C}{=}CHCOC_6H_5 \xrightarrow{NH_3} \text{XIV} \xrightarrow{HCl} C_6H_5CO\underset{\underset{OH}{|}}{C}{=}CHCOC_6H_5$$

XIV

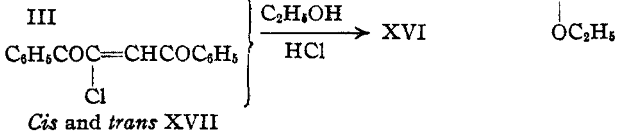
which gave benzoic acid, phenylglyoxylic amide, and a small amount of phenylglyoxylic acid. Hydrolysis with acids gives dibenzoylethenol.

While we believe that the two solid enol forms of diphenylbutanetrione are stereoisomers of dibenzoylethenol and that in solution they are in equilibrium, it would appear, nevertheless, that enolization in the other possible sense, namely, VII, is involved in some of the reactions, notably that with absolute methyl or ethyl alcoholic hydrogen chloride (or sulfuric acid). These interactions result in the formation of the new enol methyl and ethyl ethers XV and XVI, the structures of which are established by ozonizations which, as described above, lead to the formation of the corresponding benzoic esters and show that the alkoxyl group is adjacent to a phenyl. The formation of these enol ethers may therefore be formulated as follows



These ethers may be obtained from a number of other compounds by the action of absolute alcoholic hydrogen chloride, namely, dibenzoylmethoxy and ethoxy-ethylenes, dibenzoylethylene oxide and chlorohydrin,[5] and diphenyldiacetoxy and acetoxychloro-furans (XVIII and XX). All of these reactions very probably pass through a common intermediate step involving the enols V and VII, and 1,4-addition of hydrogen chloride to VII. The two methyl and ethyl ethers are easily transformed one into the other by means of the corresponding alcohol and hydrogen chloride, and are converted back into the enol upon hydrolysis with alcoholic sodium hydroxide.

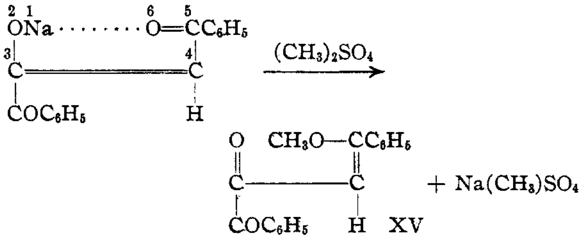
In connection with these experiments we have found to our surprise that dibenzoylacetylene III and the *cis* and *trans* dibenzoylchloroethylenes XVII react with absolute ethanolic hydrogen chloride to give largely the ethyl ether XVI, although in 95% ethanol the products are chiefly dibenzoyldichloroethane and diphenyldichlorofuran XIX.[6]



Cis and *trans* XVII

The *dl* and *meso* dibenzoyldichloroethanes are stable under the reaction conditions involved and would have been isolated if formed. It would appear therefore that, if hydrogen chloride has added during the reaction (as would be expected), it has done so in a new sense to give the keto chloride $C_6H_5COCCl_2CH_2COC_6H_5$. Such an intermediate substance has not been isolated; however, if formed under the circumstances, it might be expected to undergo alcoholysis and transformation into the stable end product XVI.

Alkylations of the sodium enolate with dimethyl and diethyl sulfates give exclusively the methyl and ethyl enol ethers XV and XVI, a result which to us was unexpected in view of the conclusions we had reached concerning the structure and configurations of the two enols. Oxygen alkylation might have been predicted in view of the behavior of α-diketones such as benzyl phenyl diketone and benzohydryl phenyl diketone,[7] but the direction in which the alkylations occurred is not one which would make these cases comparable. It is possible to account for the results either through a tautomeric equilibrium between two structurally isomeric enolates, in which chelation may be involved and perhaps facilitate the rearrangement, or by assuming that the sodium enolate actually has the structure corresponding to VII rather than V. However, in either case, oxygen alkylation of the enolate of a β-diketone system would be involved, a reaction which is inconsistent with the behavior of ordinary β-diketone enolates. An alternative hypothesis involving the dibenzoylethenol formulation V is the 1,6-addition (or reaction) of dialkyl sulfate at the ends of the system numbered in the following formula



This hypothesis is based on the interpretation of oxygen and carbon alkylations of metal enolates in terms of 1,2- and 1,4-additions to the system C=C—O—Na.[8]

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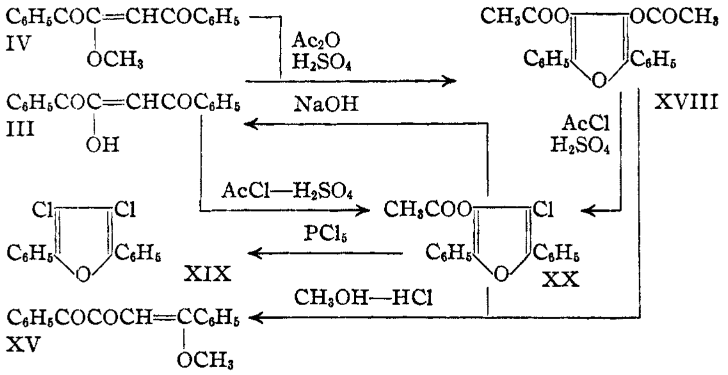
[5] Lutz and Wilder, THIS JOURNAL, **56**, 1987 (1934).

[6] Lutz and Wilder, *ibid.*, **56**, 1193 (1934).

[7] *Cf.* Kohler and Barnes, *ibid.*, **56**, 211 (1934); Kohler and Weiner, *ibid.*, **56**, 434 (1934).

[8] This system, involving conjugation between a double bond and the reactive O-Na linkage, is regarded as capable of reacting at the ends, and is in this respect somewhat analogous to allylic systems involving conjugate reduction [see Klages, *Ber.*, **39**, 2587 (1906); Lutz and Small, THIS JOURNAL, **54**, 4715 (1932); **56**, 1738, 1741 (1934); Lutz, *ibid.*, **56**, 1378 (1934)] and to the abnormal reactions of benzyl- and allylmagnesium halides with carbonyl compounds [*cf.* Johnson, *ibid.*, **55**, 3029 (1933)]. *Cf.* Hantzsch, *Ber.*, **43**, 3053

As a typical unsaturated 1,4-diketone, the enol (presumably dibenzoylethenol) reacts with acetic anhydride and sulfuric acid to give 2,5-diphenyl-3,4-diacetoxyfuran XVIII, and with acetyl chloride and sulfuric acid to give 2,5-diphenyl-3-acetoxy-4-chlorofuran XX. The enol ether, dibenzoylmethoxyethylene, reacts also with acetic anhydride and sulfuric acid, giving the diacetoxyfuran XVIII, involving however replacement of the methoxyl group with acetoxy. The isomeric methyl ether XV does not undergo this reaction which is typical only of the unsaturated 1,4-diketone types.



The structure of the two furans XVIII and XX are clear from the mode of formation and the analogy between these reactions and those of typical unsaturated 1,4-diketones and para quinones;[9] ozonization gives nearly two equivalents of benzoic acid and a small amount of oxalic acid.

One of the acetoxy groups of diphenyldiacetoxyfuran XVIII is easily replaced with chlorine by the action of acetyl chloride and sulfuric acid: the second acetoxy group is also replaceable with chlorine but only under considerably more drastic conditions with phosphorus pentachloride, giving diphenyldichlorofuran XIX (known[1,6]). Both the diacetoxy and the acetoxychlorofurans (but not the dichlorofuran) are readily hydrolyzed by means of sodium methylate with fission of the furan ring, regenerating dibenzoylethenol. Methanolic hydrogen chloride likewise in both cases splits the furan ring giving the enol methyl ether XV as the end-product.

Further studies in this field are in progress in this Laboratory.

Experimental Part

1,2-Dibenzoylethenol (V).—Dibenzoylacetylene (5 g.) was added at room temperature with stirring to 38 cc. of 92% methanol containing 0.7 g. of dissolved sodium. The mixture was then heated for five minutes at 60° and evaporated under reduced pressure. The yellow solid residue (the sodium salt) was dissolved in a large volume of hot water and the solution filtered, cooled and acidified. The enol was liberated as an oil which solidified; yield 4.2 g. (79%).

The preparation starting with dibenzoyldibromoethane was similar except that three equivalents of sodium were used and the mixture was stirred at room temperature for thirty minutes and then heated for five minutes at 60°.

In typical preparations carried out as above at room temperature or at 40°, and subsequently cooled, dibenzoylmethoxyethylene crystallized in yields varying from 50–80%, and from the filtrates small amounts of the enol were obtained.

The colorless form of the enol crystallizes from 80–95% ethanol as colorless diamond or rectangular scales which dissolve to give deeply yellow solutions. It melts at 88–89° (corr.) to a yellow liquid which on cooling and solidifying remelts at 66–67° (corr.); this is a characteristic test. Titration by the K. Meyer method at −4° in ethanol showed complete enolization.

Anal. Calcd. for $C_{16}H_{12}O_3$: C, 76.2; H, 4.8. Found: C, 76.2, 76.2; H, 4.8, 4.8.

The yellow isomeric enol was prepared by fusing the colorless isomer on the steam-bath and cooling the brilliant yellow melt which crystallized in yellow balls of radiating needles or scales. It is best recrystallized from petroleum ether; m. p. 68° (corr.). The K. Meyer titration at −4° in ethanol showed complete enolization.

Anal. Calcd. for $C_{16}H_{12}O_3$: C, 76.2; H, 4.8. Found: C, 76.1, 76.0, 76.2; H, 4.9, 4.8, 4.8.

A discussion of some of the properties of the two enols has already been given in the introduction.

The sodium enolate of 1,4-diphenyl-1,2,4-butanetrione is obtained as a yellow crystalline powder and on recrystallization from ethanol gives yellow needles which are sparingly soluble in water.

Anal. Calcd. for $C_{16}H_{11}O_3Na$: C, 70.2; H, 4.0. Found: C, 70.1; H, 4.1.

Copper Salt.—Greenish crystalline powder.

Anal. Calcd. for $C_{32}H_{22}O_6Cu$: C, 68.0; H, 3.9; Cu, 11.2. Found: C, 68.0; H, 3.8; Cu, 11.3.

Hydrolytic Cleavage of Dibenzoylethenol.—A suspension of the enol in aqueous barium hydroxide was distilled; acetophenone was isolated in the steam distillate and was identified as the phenylhydrazone by a mixed melting point with an authentic sample. The barium hydroxide solution on acidification and extraction with ether gave phenylglyoxylic acid of m. p. 62–63° (identified as phenylhydrazone, m. p. 166°, and semicarbazone, m. p. 202° dec.).

Ozonization of Dibenzoylethenol.[10]—A stream of ozonized oxygen was passed for two hours through a

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(1910); and Sidgwick, *J. Chem. Soc.*, **127**, 907 (1925); also Robinson, *ibid.*, 109 (1916). The reaction between chloroform and sodium *m*-cresolate [Auwers, *Ber.*, **35**, 4207 (1902)] may be interpreted in similar terms as a 1,6-addition of Cl and $CHCl_3$ at the ends of the system Na—O—C=C—C=C.

(9) Lutz, THIS JOURNAL, **48**, 2916 (1926).

(10) *Cf.* Sheiber and Herold, *Ann.*, **405**, 295 (1914).

solution of 3 g. of the enol in 25 cc. of dry chloroform (ice-bath). The solvent was evaporated in a current of air (without exclusion of moisture) and the residue was taken up with water. The mixture was heated to boiling, cooled, treated with an excess of sodium bicarbonate, and extracted with ether (ten times), giving 0.45 g. of non-acidic oil. The aqueous solution was acidified, cooled and the benzoic acid filtered out (yield 1.05 g. or 73%). The filtrate was extracted with ether (five times), yielding an oil which was taken up in water. A small amount of impure benzoic acid crystallized at this point and was filtered off. The solution was treated directly with an excess of semicarbazide hydrochloride and the phenylglyoxylic acid semicarbazone precipitated (2.2 g. or 85%). The non-acidic oil (above) was vacuum distilled at 80°; a small amount of colorless oil collected on the cold finger condenser, leaving considerable non-volatile resin. The distillate, dissolved in ethanol and treated with phenylhydrazine, gave 0.1 g. of phenylglyoxal osazone of m. p. 149–150° (identified by a mixed melting point with an authentic sample).

Ozonization of dibenzoylmethoxyethylene (3 g.), carried out as above, gave 0.84 g. of benzoic acid (62% of one equiv.) and 0.13 g. of phenylglyoxylic acid semicarbazone (5.5% of one equiv.). The oily non-acidic fraction containing the phenylglyoxylic ester was hydrolyzed by short refluxing with aqueous sodium hydroxide, the phenylgloxylic acid being isolated by extraction with ether, and conversion as above into the semicarbazone (yield 2.05 g., 88% of one equiv.).

Ozonization of dibenzoylethylene (2.6 g.), as above, gave 1.97 g. of benzoic acid (80% of two equiv.), 0.2 g. of phenylglyoxylic acid semicarbazone (4.5% of one equiv.), and a trace of phenylglyoxal (as the osazone). Ozonization in 94% acetic acid gave a 25% yield of phenylglyoxal (isolated as the osazone); the crude oily product had an unmistakable odor of benzaldehyde.

The action of alcoholic sodium acetate (standing or short heating) on dibenzoylacetylene, dibenzoyldibromoethane, or on dibenzoylethenol gives an amorphous yellow product (*cf.* Refs. 1 and 2). From this, if conditions during the reaction are not too drastic, a yellow crystalline product (m. p. 167–168°) (dec.) may be obtained and crystallized from chloroform and ligroin. Analysis indicated it to be $C_{32}H_{22}O_5$ (or a polymer) (Calcd.; C, 79.0; H, 4.60. Found: C, 79.0, 79.0; H, 4.5, 4.5).

The Action of Diazomethane on the Enols.—When either enol, as a solid, is added to an ether solution of a slight excess of diazomethane at −10 to +10°, vigorous reaction occurs with the evolution of nitrogen. On evaporation an oil is obtained from which yields of 50–65% of dibenzoylmethoxyethylene are obtained on crystallization from methanol. The rest of the material is a viscous yellow oil. Variations in the procedure, including the use of petroleum ether as the solvent,[11] did not improve the yields nor reveal any new crystalline product.

Hydrolysis of dibenzoylethenol methyl and phenyl ethers with a slight excess of sodium hydroxide in 92% methanol by heating for five minutes at 60°, gave dibenzoylethenol, isolated as above, in yields as high as 90%.

Replacement of the methoxyl of dibenzoylmethoxyethylene with ethoxyl was accomplished by refluxing for one hour an absolute ethanol solution of one equivalent each of sodium 3-methylphenolate and dibenzoylmethoxyethylene. From the resinous product approximately 15% yields each of unchanged material and dibenzoylethoxyethylene were isolated by fractional crystallization from ethanol (identified by mixed melting points). A sample of dibenzoylmethoxyethylene was recovered unchanged when refluxed for nine hours with methanolic sodium phenolate.

Inversion of Dibenzoyl-3-methylphenoxyethylene.—An ethanol solution of the *trans* isomer (yellow in the fused state or in solution) of m. p. 95° was bleached in strong sunlight in two hours and gave a nearly quantitative yield of the colorless *cis* form of m. p. 103° (identified by mixed melting point).

1,2-Dibenzoylaminoethylene (VI) was prepared by refluxing a solution of dibenzoylmethoxyethylene in alcoholic ammonia (*cf.* Ref. 2). A high melting compound (m. p. 170°, dec.) was obtained in small yield, but as the main product when large amounts of water were present during the reaction. Hydrolysis of the dibenzoylaminoethylene by refluxing with 6 *N* hydrochloric acid to which alcohol was added, gave dibenzoylethenol in yields averaging 75%.

Ozonization of 4 g. (carried out as above) gave 1.5 g. of benzoic acid (82% of one equiv.) and 0.4 g. of phenylglyoxylic acid semicarbazone (12% of one equiv.). The non-acidic fraction (resinous) was extracted with hot water which on cooling gave 0.4 g. (17%) of phenylglyoxylic acid amide (m. p. 76–77°); this was identified by analysis (calcd. for $C_8H_7O_2N$, C, 64.4; H, 4.7. Found: C, 63.9; H, 4.9) and conversion into the semicarbazone. The aqueous filtrate, treated directly with semicarbazide hydrochloride, gave 0.85 g. (26%) of phenylglyoxylic acid amide semicarbazone (m. p. 215–217°). The total yield of phenylglyoxylic acid amide isolated as such or as the semicarbazone was 43% of one equivalent. The residue of material was resinous.

Phenylglyoxylic Acid Amide Semicarbazone, $C_6H_5C({=}NNHCONH_2)CONH_2$.—Crystallized as short square-ended prisms from ethanol in which it is difficultly soluble; m. p. 233–234° (corr., dec.).

Anal. Calcd. for $C_9H_{10}N_4O_2$: C, 52.40; H, 4.89. Found: C, 52.64; H, 4.80.

1,4-Diphenyl-4-methoxy-3-butene-1,2-dione, XV.—This enol ether is obtained in 90–95% yield by the action of methanolic hydrogen chloride on any of the following: dibenzoylmethoxy and ethoxyethylenes, and 1,4-diphenyl-4-ethoxy-3-butene-1,2-dione. The procedure is to suspend 10 g. of the substance in 100 cc. of absolute 20% methanolic hydrogen chloride, and allow the mixture to stand at room temperature for twenty-four hours. Refluxing with methanolic hydrogen chloride acts in a similar way but with poorer yields. In a typical case sulfuric acid was substituted for hydrogen chloride with a similar result. In general the product was recovered from the methanolic hydrogen chloride solution by evaporation in a current of dry air at room temperature, preferably under diminished pressure, washing the residue with water, and crystallizing from alcohol; m. p. 108–109° (corr.).

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(11) Method of Meerwein, *Ber.*, 61, 1840 (1928).

The methyl ether XV was obtained also by refluxing a mixture of 25 cc. of methanol, 6 cc. of dimethyl sulfate, and 5 g. of the sodium enolate of diphenylbutanetrione for one hour. The resulting red solution on cooling deposited the methyl ether in 90% yield.

Anal. Calcd. for $C_{17}H_{14}O_3$: C, 76.69; H, 5.30. Found: C, 76.38; H, 5.30.

On treatment with ethanolic hydrogen chloride this methyl ether is converted nearly quantitatively into the ethyl ether.

The methyl ether is stable when heated at 225° for twenty minutes and can be sublimed in the vacuum oven. It is unaffected by the following: boiling acetic anhydride, cold acetic anhydride and sulfuric acid (it is resinified on heating), boiling acetyl chloride, and acetyl chloride with sulfuric acid (refluxing gives resins). The action of phenylhydrazine gives only resins. The action of zinc dust and glacial acetic acid at varied temperatures gives only unchanged material and resinous products. Hydrolysis with sodium methylate (heating in methanol solution for fifteen minutes) gives dibenzoylethenol and some unchanged material.

A mixture of 1 g. of the methyl ether with 2 g. of phosphorus pentachloride and 5 cc. of phosphorus oxychloride was allowed to stand for one hour at room temperature. Hydrolysis in ice gave a product which was recrystallized from ethanol (95% yield) and identified by mixed melting point as diphenyldichlorofuran.

Ozonization of 20 g. (3 portions) in chloroform for ten to twelve hours with subsequent evaporation in a current of moist air under partially reduced pressure gave an oily residue which was extracted with sodium carbonate solution and ether. From the sodium carbonate solution 7.2 g. of benzoic acid was recovered (a yield of 78% of one equivalent). The ether solution was distilled giving a 58% yield of methyl benzoate of b. p. 197–199° which was further identified by hydrolysis to benzoic acid.

1,4-Diphenyl-4-ethoxy-3-butene-1,2-dione, XVI.—The enol ethyl ether is prepared in the same way as the methyl ether, in 90–95% yields, using absolute ethanol containing 20–25% of hydrogen chloride, from dibenzoylethenol, dibenzoylmethoxy and ethoxyethylenes, dibenzoylethylene oxide and chlorohydrin (and the unstable chlorohydrin obtained from them by the action of ethereal hydrogen chloride), dibenzoylacetylene, *cis* and *trans* dibenzoylchloroethylenes, and 1,4-diphenyl-4-methoxy-3-butene-1,2-dione. In a typical case, namely, dibenzoylmethoxyethylene, sulfuric acid was substituted for hydrogen chloride with similar results. The product was recrystallized from ethanol, m. p. 96° (corr.).

Anal. Calcd. for $C_{18}H_{16}O_3$: C, 77.1; H, 5.7. Found: C, 76.9; H, 5.7.

Hydrolysis by means of boiling sodium methylate solution gave dibenzoylethenol. The ethyl ether reacts more readily with this reagent than does the methyl ether XV. Unchanged material and resins are obtained on attempted **reduction** with zinc and glacial acetic acid. **The action of phosphorus pentachloride** at room temperature in phosphorus oxychloride solution, and subsequent hydrolysis in ice and recrystallization of the product from ethanol, resulted in an 80% yield of diphenyldichlorofuran (identified by mixed melting point). **With phosphorus pentabromide** a 50% yield of di-(*p*-bromophenyl)-dibromofuran was obtained. **Ozonization** in chloroform (as with the methyl ether) gave benzoic acid (yield over 50% of one equivalent) and ethyl benzoate (91% of one equivalent, identified by b. p. 208–212°, and hydrolysis to benzoic acid). Considerable tar was left from the distillation of the latter.

2,5-Diphenyl-3-chloro-4-acetoxyfuran (XX) was prepared by the action of acetyl chloride and sulfuric acid (the usual procedure) on dibenzoylethenol or on 2,5-diphenyl-3,4-diacetoxyfuran. Recrystallized from alcohol and from ethyl acetate–petroleum ether mixtures, m. p. 132° (corr.).

Anal. Calcd. for $C_{18}H_{13}O_3Cl$: C, 69.10; H, 4.19; Cl, 7.35. Found: C, 68.93; H, 4.24; Cl, 7.40.

Hydrolysis of 0.5 g. with a solution of 0.2 g. of sodium in 10 cc. of methanol at room temperature gave 0.3 g. of dibenzoylethenol, isolated by evaporation (air blast), solution of the residual sodium salt in water, and acidification.

2,5-Diphenyl-3,4-diacetoxyfuran, XVIII.—One gram of dibenzoylethenol reacted at room temperature with acetic anhydride containing a few drops of sulfuric acid, giving a dark colored solution which was decomposed in water. The residue was crystallized from alcohol, giving 0.8 g. of the diacetoxyfuran. Dibenzoylmethoxyethylene reacts in the same way. Crystallized from ethyl acetate and ligroin, m. p. 139–139.5° (corr.).

Anal. Calcd. for $C_{20}H_{16}O_5$: C, 71.40; H, 4.79. Found: C, 70.91; H, 4.85.

Hydrolysis of 1 g. with sodium ethylate (room temperature) gave 0.4 g. of dibenzoylethenol.

The 1,4-Di-(*p*-chlorophenyl)- and Di-(*p*-bromophenyl)-1,2,4-butanetrione Enols.[12]—These two enols have been made from the corresponding diaroyl-dibromoethanes with methanolic sodium hydroxide, but each exists only in one form which is yellow. From their solubilities, they appear to be chelated. They are probably *trans* di-(*p*-halogenobenzoyl)-ethenols. However, with diazomethane they react to give intractable oils and none of the easily crystallizable colorless di-(halogenobenzoyl)-methoxyethylenes which are known.[2,6]

Di-(*p*-chlorobenzoyl)-ethenol, $ClC_6H_4COCH{=}C(OH)COC_6H_4Cl$.—The enol was prepared by the action of a solution of 3 equivalents of sodium in 90–95% methanol on di-(chlorobenzoyl)-dibromoethane (heating to boiling). The alkaline solution, diluted with water, was extracted with ether to remove small amounts of di-(chlorobenzoyl)-methoxyethylene, and acidified, liberating the crude enol as a resin which was crystallized from chloroform or acetone as pale yellow needles of m. p. 154°; yield about 50%.

Anal. Calcd. for $C_{16}H_{10}O_3Cl_2$: C, 59.83; H, 3.14; Cl, 22.1. Found: C, 60.17; H, 3.1; Cl, 22.25.

Di-(*p*-bromobenzoyl)-ethenol, $BrC_6H_4COCH{=}C(OH)COC_6H_4Br$.—Prepared as was the above analog. When considerable amounts of water are present, and heating is prolonged, *p*-bromobenzoic acid is obtained also; crystallized as difficultly soluble yellow needles of m. p. 171°.

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[12] The previously reported substance prepared by the action of sodium acetate on di-(bromobenzoyl)-dibromoethane is a complex mixture of condensation products analogous to that obtained in the dibenzoyl series (see Ref. 1a).

Anal. Calcd. for $C_{16}H_{10}O_3Br_2$: C, 46.74; H, 2.46; Br, 38.9. Found: C, 47.1; H, 2.44; Br, 38.9.

Summary

The synthesis of 1,4-diphenylbutane-1,2,4-trione enol is described. The enol exists in two forms which are regarded as stereoisomers of dibenzoylethenol. The structures and configurations are discussed on the basis of a preliminary study which includes isomerization, hydrolysis, ozonization and alkylation with diazomethane.

The structure, configurations, and some reactions of the dibenzoylethenol ethers are considered.

The formation and hydrolysis of dibenzoylaminoethylene is described and the structure established by ozonization.

The alkylation of 1,4-diphenylbutane-1,2,4-trione enol by alcohol and acids and by means of dialkyl sulfates leads to the enol alkyl ethers of 1,4-diphenyl-1,2-diketo-3-butene-4-ol, rather than of dibenzoylethenol. The reactions and determination of structure of these ethers are considered.

The enol reacts with acetic anhydride and acetyl chloride (with sulfuric acid) like a typical unsaturated 1,4-diketone, giving furans.

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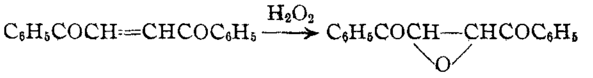
Dibenzoylethylene Oxide and Chlorohydrin

BY ROBERT E. LUTZ AND FRANK N. WILDER

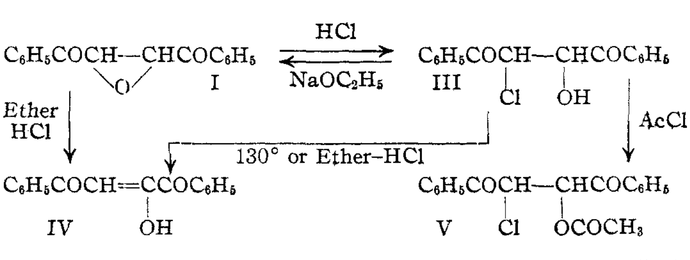
Dibenzoylethylene oxide II is of interest as an oxido-1,4-diketone and because of its relation to saturated and unsaturated 1,4-diketones and the 1,2,4-triketones, particularly with respect to a convenient method of preparing dibenzoylethenol IV.[1] It is prepared from both *cis* and *trans* dibenzoylethylenes I by the action of hydrogen peroxide



$$C_6H_5COCH{=}CHCOC_6H_5 \xrightarrow{H_2O_2} C_6H_5COCH{-}CHCOC_6H_5$$

I *Cis* and *trans* II

and is transformed by means of ethereal hydrogen chloride into dibenzoylethenol IV, and by hydrochloric acid in 80% ethanol into the chlorohydrin III. The chlorohydrin is stable under ordinary conditions and gives a monoacetyl derivative (V); when heated at 130° it gives dibenzoylethenol and hydrogen chloride; the action of sodium ethylate converts it back into the oxide. These various reactions are typical and establish the structures of both the oxide and chlorohydrin.



The mechanism of the transformation of dibenzoylethylene oxide into dibenzoylethenol by the action of ethereal hydrogen chloride probably involves the chlorohydrin III which is similarly converted into the ethenol under these conditions. A different and unstable chlorine containing compound is isolated, however, on evaporation at room temperature of the ethereal hydrogen chloride solutions resulting from the action of this reagent both on the chlorohydrin and also on the enol. This product is apparently a hydrogen chloride addition compound of the enol IV or its tautomer, $C_6H_5COCOCH{=}C(OH)C_6H_5$; it loses hydrogen chloride spontaneously on standing or on warming with solvents to give dibenzoylethenol; it gives no simple derivatives and reacts in the same sense as dibenzoylethenol and hydrogen chloride, the products of spontaneous decomposition. When heated for a short time with methyl or ethyl alcohol it is converted into the enol ethers, $C_6H_5COCOCH{=}C(OR)C_6H_5$. The latter are obtained also directly from the oxide and from the enol[1] by the action of alcoholic hydrogen chloride.

Both the chlorohydrin III and its acetate V react with acetyl chloride and sulfuric acid to give 2,5-diphenyl-3,4-dichlorofuran VI which is known.[2]

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[1] Lutz, Wilder and Parrish, THIS JOURNAL, **56**, 1980 (1934).

[2] Conant and Lutz, *ibid.*, **47**, 881 (1925). The action of acetic anhydride and sulfuric acid gives, instead of diphenylacetoxychlorofuran, a new product which is now under investigation.