

The distribution functions possess maxima characteristics similar to those previously discussed for " $r = 1$ " polymers. In fact, the same equations may be used for locating the x_{\max} value for Π_x by replacing p with $r^{1/2}p$. Exact equations for M_w and M_z , corresponding to equations (13) and (14), are cumbersome; for all practical purposes it is permissible merely to replace p with $r^{1/2}p$ in (13) and (14), respectively. It follows that here also the ratio of $M_n:M_w:M_z$ approaches 1:2:3 for high molecular weights. Thus, sedimentation equilibrium measurements in the ultracentrifuge would not distinguish the two types of polymers.

The author wishes to acknowledge his gratitude to Dr. Wallace H. Carothers for his valuable advice and keen interest in this work. The author is also indebted to Dr. E. O. Kraemer for reading and criticizing the manuscript.

Summary

1. Equations expressing the weight fraction, number, and mole fraction of each molecular species in a linear condensation polymer have been derived on the basis of simple and not improbable assumptions. The characteristics of these functions have been demonstrated and discussed.

2. The number-average, weight-average and Z-average molecular weights of Lansing and Kraemer are shown to be in the ratio 1:2:3 for the high molecular weight polymers. The bearing of this result on Staudinger's method for determining molecular weights has been discussed.

3. The special case of polymers prepared by the condensation of non-equivalents of two bi-functional reactants (A—A + B—B) has been analyzed and shown to conform to a distribution similar to the above. Other special cases can be subjected to a similar analysis.

WILMINGTON, DEL.

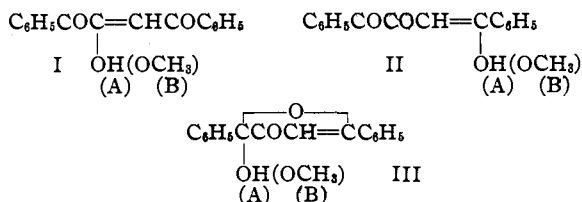
RECEIVED MARCH 24, 1936

[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY OF THE UNIVERSITY OF VIRGINIA]

Further Studies on 1,4-Diphenyl-1,2,4-butanetrione Enol, Including Alkylation and Benzoylation

BY ROBERT E. LUTZ AND ALFRED H. STUART

Two methyl ethers have been obtained from the enol. One of these, dibenzoylmethoxyethylene I(B), the structure of which is certain, was made directly by the action of diazomethane.^{1b} The other, a structural isomer II(B) or III(B), was obtained by the action of methanol and acid on the enol or various of its derivatives and was believed to have the open chain structure II(B) because it gave methyl benzoate on ozonization;^{1b} however, the alternative cyclic structure III(B),² which was not considered at that time, also would account for this result.

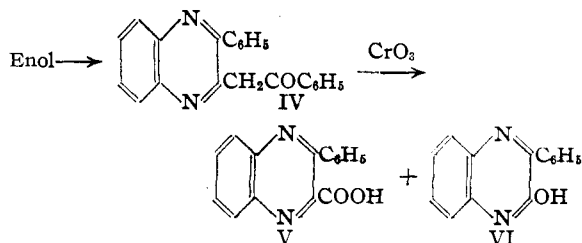


(1) Cf. (a) Lutz, *THIS JOURNAL*, **56**, 1590 (1934); (b) Lutz, Wilder and Parrish, *ibid.*, **56**, 1980 (1934); Lutz and Wilder, *ibid.*, **56**, (c) 1987, (d) 2065, (e) 2145 (1934).

(2) Cf. (a) Blatt, *ibid.*, **57**, 1103 (1935); (b) Kohler, Westheimer and Tishler, *ibid.*, **58**, 264 (1936).

The ease of formation of the isomeric ether by catalytic etherification does not distinguish between the two formulations II(B) and III(B) since there is analogy for the reaction in both open chain and cyclic types (*cf.* hydroxynaphthoquinone³ and the sugars). The quinoxaline reaction, however, which is specific for α -diketones, has been used.^{2a}

o-Phenylenediamine reacts readily with the enol to give a quinoxaline (IV) which is bright orange in color in contrast with other quinoxalines of this series. Oxidation of this product by means of chromic acid gives the carboxy and



(3) Fieser, *ibid.*, **48**, 2922, 3201 (1926).

hydroxy quinoxalines V and VI.⁴ The structure of IV seems to be established adequately by these reactions; however, the color is not accounted for.

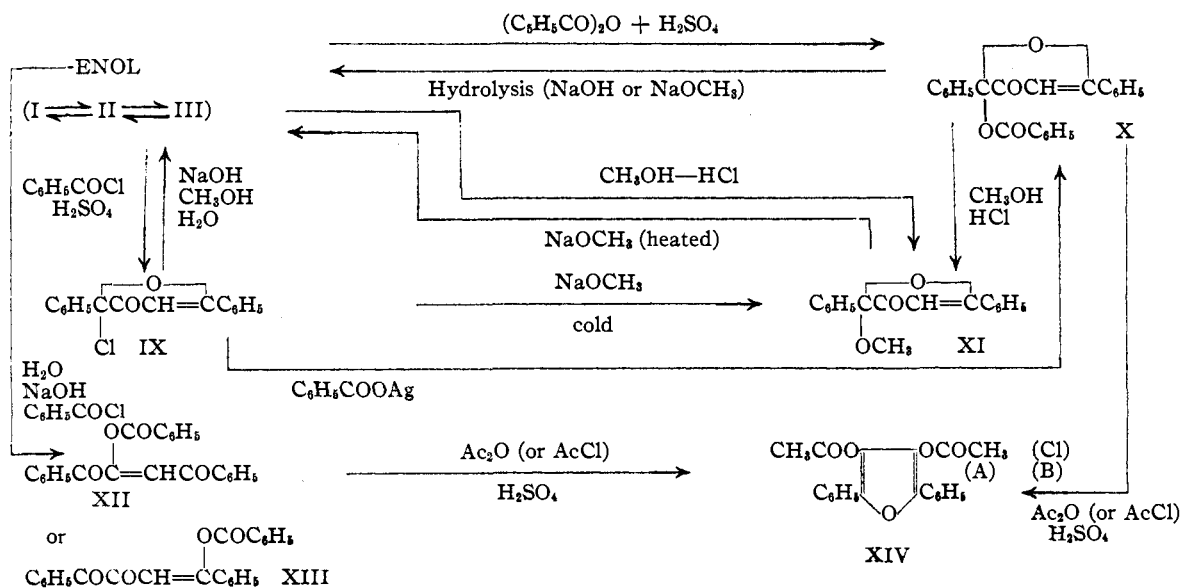
Dibenzoylmethoxyethylene I(B), the structurally isomeric ether, and dibenzoylamino and chloroethylenes (VII and VIII) do not react under ordinary conditions with *o*-phenylenediamine. However, under more drastic conditions, namely, long continued refluxing with the reagents, dibenzoylmethoxyethylene gives IV with elimination of the methoxyl group, a reaction involving either the conjugated system or hydrolysis first to the reactive enol (the ether is known to be hydrolyzed or ammonolyzed easily).^{1b} Dibenzoylaminoethylene VII under these conditions reacts very slowly giving IV, but the isomeric ether II or III(B) and also the *trans* chloro compound VIII, are stable.



In regard to the bearing of these facts on the structure of the isomeric ether, the α -diketone formula II(B) seems to be excluded by the failure to react with *o*-phenylenediamine even under drastic conditions, and the cyclic formula III(B) is therefore the correct one. Other properties¹ of the ether support this conclusion:

duced by sodium hydrosulfite or zinc and acetic acid under ordinary conditions as would be expected of an α -diketone; (c) it does not react with acetyl chloride or acetic anhydride and sulfuric acid under ordinary conditions (as does dibenzoylmethoxyethylene I(B) and as presumably would an ether of formula II(B)); and (d) it is only slowly hydrolyzed with alkali whereas the true enol ether, dibenzoylmethoxyethylene, and the two analogous 2- and 4-methoxynaphthoquinones³ are hydrolyzed very rapidly under these conditions.

The chloro compound obtained by the action of thionyl chloride on either the enol or its methyl ether I(B) was previously assumed to be $\text{C}_6\text{H}_5\text{CO}-\text{COCH}=\text{C}(\text{Cl})\text{C}_6\text{H}_5$.^{1c} This compound must have the cyclic structure IX, however, in view of the following facts: (a) it is colorless; (b) it reacts readily with *o*-phenylenediamine to give the quinoxaline IV; (c) the chlorine is reactive as shown by the ease with which it is eliminated in the quinoxaline reaction and also in methanolysis to the cyclic ether III(B); and (d) the chlorine is replaceable readily by methoxyl by means of cold sodium methylate, giving the cyclic ether III(B) under conditions wherein the open chain enol ether I(B) is hydrolyzed directly to the enol.



(a) the ether is colorless in contrast to other known α -diketones (the dimesityl analog of II(B) is bright yellow);⁵ (b) it is not easily re-

(4) We are indebted to Dr. A. H. Blatt for furnishing samples of V and VI for purposes of identification.

(5) Lutz and Wood, unpublished results.

Acetylation of the enol with acid^{1b} or with pyridine as catalyst leads to the furans XIV (A and B). Studies on the enol salts, however, led to intractable products.

The action of benzoyl chloride and sulfuric

acid on the enol gave the cyclic chloro compound IX instead of the expected furan of the type XIV(B). Benzoic anhydride and sulfuric acid likewise failed to give the benzoyl analog of the furan XIV(A), but instead gave a cyclic benzoate X the structure of which follows from its synthesis from the cyclic chloro compound IX by means of silver benzoate, and from its failure to react with *o*-phenylenediamine, in contrast with the open chain enol benzoate XII which reacts readily. The cyclic benzoate (X) is very reactive as would be expected; methanolic hydrogen chloride converts it into the cyclic methyl ether XI, sodium methylate hydrolyzes it quickly to the enol, and acetic anhydride or acetyl chloride with sulfuric acid converts it into the diacetoxy or acetoxychlorofurans XIV (A) or (B).

Benzylation of the sodium salt of the enol in aqueous alkaline medium gives yields as high as 50% of the enol benzoate. The nature of this product is evident from the ease of hydrolysis to the enol and benzoic acid by means of cold alkali. Of the two possible formulas, XII and XIII, the former is the more likely, particularly in view of the absence of color. It reacts readily with *o*-phenylenediamine giving the quinoxaline IV, with methanolic hydrogen chloride to give the cyclic ether XI, and with acetic anhydride or acetyl chloride and sulfuric acid to give the diacetoxy and acetoxychlorofurans XIV(A) or (B). The ease of replacement of benzoyl by acetyl shows that neither this reaction nor the analogous conversion to a β -benzoyloxyfuran could be used to distinguish between the two structures XII and XIII. Preliminary reduction experiments with this end in view have not been successful.

There was produced consistently in the benzylation of the sodium enolate in isopropyl ether as solvent smaller yields (30% or less) of the enol benzoate XII together with 20–25% yields of a product derived from the carbon benzoyl compound. The studies of the latter series are not yet completed and will be the subject of a later paper.

We have evidence that the true open chain enol methyl ether II(B), which we have not yet been able to isolate and characterize, is formed in considerable amount during methylation of the enol with diazomethane. Both forms of the enol react similarly, even in petroleum ether,

solvent conditions under which they appear to be reasonably stable. The yields of dibenzoylmethoxyethylene I(B) average 30–50%. The oily product at the beginning contains no unchanged enol as shown by the absence of the very characteristic red ferric chloride test. However, in the course of handling the crude mixtures in order to isolate the dibenzoylmethoxyethylene, free enol is regenerated, gives a strong ferric chloride test, and has been isolated in one instance. The quinoxaline test on these oils gave amounts of IV corresponding to total yields of about 15–30% (neither the ethers I(B) nor III(B) react under these conditions). These facts indicate the presence of an unstable enol derivative which is readily hydrolyzed to the enol and which appears to be the open chain ether II(B). This hypothesis is not unreasonable in view of the fact that the analog has since been isolated in the dimesityl series.⁵ Further evidence for the presence of this compound in approximately the amounts indicated above was obtained by ozonizing the crude product after separation of the dibenzoylmethoxyethylene and isolating methyl benzoate in a yield of 20%. The cyclic ether III(B), if present, would have given this result, but it could hardly have been formed as a result of methylation of III with diazomethane; furthermore, it crystallizes easily, has never been isolated in this type of methylation, and could not possibly have been present in amounts sufficient to account for the above result. It seems to be established, therefore, that the ether II(B) as well as I(B) is formed in the methylation of the enol with diazomethane, and that the enol reacts partly in the sense of formula II(A) as well as I and III(A).⁶

The foregoing facts necessitate reconsideration of the structural relations of the two solid forms of the enol. Both isomers react readily and similarly with one equivalent of bromine, and with ferric chloride, in ethanol at -10 – 15° , and with diazomethane in petroleum ether, solvent conditions under which the two forms alone appear to be fairly stable. It is not certain, however, that they are both true enols in view of the great mobility of the equilibrium and probable catalytic effect of the reagents, and

(6) In this connection it is noteworthy that since phenylglyoxylic acid was not found in significant amounts in the above ozonization of II(B), the discussion of results in the first paper (end of p. 1781, ref. 1b) is valid even though the methyl ether then under consideration (formula VIII of that paper) was really the cyclic compound III(B).

since a cyclic compound such as III(A) might react with bromine in much the same sense as the enol. The hypothesis that the two forms are *cis-trans* enols^{1b} is unlikely, particularly in view of the fact that on methylation with diazomethane they give the same mixtures of the two structural and not stereoisomeric methyl ethers. The properties of the yellow form are in accord with an assumption of chelation between I(A) (*trans*) and II(A), with the possibility of actual existence of both isomers minimized or eliminated (through resonance). The colorless form can hardly be the triketone or the enol II(A) in view of the absence of color. The cyclic formulation III(A) for this isomer is the most reasonable one since, coupled with the assumption of chelation in the yellow form, it explains adequately why the two isomers always give the same results on methylation with diazomethane.

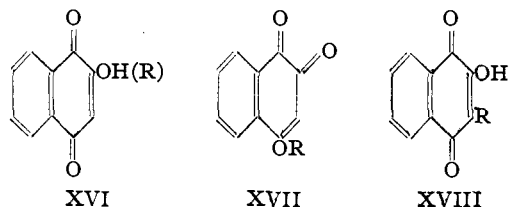
The formation of the cyclic ether III(B) upon alkylation of the sodium salt with dimethyl sulfate (reported in an earlier paper^{1b}) was found to result not from direct alkylation but from hydrolysis of the sodium salt and catalytic etherification of the resulting enol through the action of alcohol and the acid generated by hydrolysis of dimethyl sulfate. In inert solvents the sodium salt does not react either with dimethyl sulfate or methyl iodide. In aqueous media, the alkylation was too slow to compete with hydrolysis of the reagent.

Alkylation was more conveniently studied using the silver salt and alkyl halides. With methyl iodide a 70% yield of the carbon-alkyl compound resulted, the gross structure of which was shown by hydrolytic fission to phenylglyoxylic acid and propiophenone. The oxygen-alkyl compound I(A) was formed also in approximately 10% yield. The new carbon-alkyl compound apparently has the cyclic structure $C_6H_5\overline{C(OH)COC(CH_3)=C_6H_5}$, XV (*cf.* ref. 2b), and will be considered in a later paper.

Ethylation of the silver salt with ethyl iodide gave a mixture from which were obtained yields of carbon- and oxygen-alkyl compounds of 50 and 20%, respectively. The carbon-alkyl compound (new) was identified by hydrolytic fission to phenylglyoxylic acid and butyrophenone. Propyl iodide also gave a carbon-alkyl product (45% yield, identified by hydrolytic fission); however, in this case we were unable to isolate a crystal-

line oxygen-alkyl compound from the residual oils.

From the above results it would appear that there is nothing strikingly abnormal in the mode of alkylation in this series, contrary to the inference previously drawn from preliminary experiments.^{1b} The yield of carbon-alkyl product, however, is relatively very high as compared with that in the alkylation of the α -diketones⁷ and hydroxynaphthoquinone.³



The analogy between the enol I(A) and hydroxynaphthoquinone XVI deserves emphasis. Both have the 1,2,4-triketone-enol system terminated by aromatic groups and both are rather strongly acidic. In both cases the silver salt is easily alkylated in contrast with the sodium salt. Hydroxynaphthoquinone gives mixtures of the two oxygen ethers XVI and XVII but does not give carbon-alkyl compounds (XVIII) with simple alkyl halides (methyl and ethyl) although considerable amounts are formed when more active unsaturated halides are used. In the case of diphenylbutanetrione enol, however, carbon-alkylation is the dominant reaction and alkylation at the enol oxygen-4 (formula IIB) was not observed although it may have occurred to a very small extent. Diazomethane reacts with hydroxynaphthoquinone to give exclusively the 2-oxygen ether, but in the case of our enol there is formed a mixture of the ethers I(B) and II(B). Catalytic etherification of I(A) leads to the formation of the cyclic ether III(B); however, with hydroxynaphthoquinone, where cyclization and chelation are excluded on steric grounds, only the 2-ether is formed. Both hydroxynaphthoquinone ethers XVI and XVII are hydrolyzed easily by alkali as are the enol ethers I(B) and II(B) (the 4-ethers in both series appear consistently to be more easily hydrolyzed than the 2-ethers). The cyclic ether III(B), in contrast with true enol ethers, is not hydrolyzed by alkali with the same degree of ease.

(7) Kohler and Barnes, *THIS JOURNAL*, **56**, 211 (1934); Kohler and Weiner, *ibid.*, **56**, 434 (1934); Barnes and Payton, *ibid.*, **58**, 1300 (1936).

Experimental Part

The experiments on the two isomeric enols were largely repetitions of earlier experiments by methods described elsewhere, and since in most cases they are referred to specifically in the foregoing discussion, details are unnecessary.

The sodium salt of the enol is best prepared by treating an alcoholic solution with the calculated amount of sodium alcoholate, the salt being obtained as a yellow precipitate which is difficultly soluble in cold water but dissolves hot and does not crystallize out on cooling. Acidification generates the yellow form of the enol.

The sodium salt yielded unchanged enol after being subjected to the action of an excess of dimethyl sulfate under a variety of conditions including refluxing in inert solvents, benzene or isopropyl ether. Similarly, practically no alkylation resulted when experiments were conducted in aqueous media under various conditions of time, temperature and alkalinity.

When the sodium salt or the free enol is treated in alcohol with an excess of dimethyl sulfate, a nearly quantitative yield of the cyclic ether III (B) corresponding to the alcohol used as solvent is obtained regardless of whether dimethyl or diethyl sulfate is used. It is obvious that the dialkyl sulfate undergoes hydrolysis and the acid generated liberates the enol and catalyzes etherification.

The silver salt of the enol was obtained as a brilliant yellow precipitate by adding 2% silver nitrate solution to a cooled aqueous solution of the sodium salt. It is somewhat unstable and often turns dark on standing and drying. *Anal.* Calcd. for $C_{16}H_{11}O_3Ag$: Ag, 30.1. Found: Ag, 30.0. Alkylation with dimethyl sulfate in methanol or ethanol gave the cyclic alkyl ether corresponding to the solvent used. Apparently the alkylation is far too slow to avoid hydrolysis, liberation of the enol and catalytic etherification.

The quinoxaline reactions were carried out by dissolving the compound and an equal weight of *o*-phenylenediamine in alcohol and heating to boiling, the product crystallizing directly or on subsequent cooling of the solution. The products were recrystallized from ethanol. The following compounds were recovered unchanged under these conditions: I(B), III(B), VII, VIII, X and XIV(A). The compounds III(B), VIII, X and XIV(A) were recovered unchanged also after four hours of refluxing with the reagent. The enol, the enol benzoate XII, the cyclic chloro compound IX and the acetoxychlorofuran XIV(B) reacted immediately on boiling, the orange crystals of the quinoxaline IV appearing directly or upon seeding. Dibenzoylmethoxyethylene after four hours of refluxing with the reagent gave IV in good yield. Under these conditions dibenzoylaminoethylene VII gave largely unchanged material, and on six hours of refluxing with the reagents gave a 40% yield of IV.

2-Phenyl-3-phenacylquinoxaline, IV, is bright orange in color, even after careful purification including distillation in the vacuum oven. It is difficultly soluble in ethanol from which it was recrystallized; melting point 169–170° (corr.). *Anal.* Calcd. for $C_{22}H_{18}ON_2$: C, 81.5; H, 4.94. Found: C, 81.3; H, 5.15.

Oxidation was carried out by treating 2 g. of IV in 10 cc. of hot concd. acetic acid with 3 g. of chromic acid

in 6 cc. of 50% acetic acid, the mixture being boiled for two minutes. The products were separated by successive extractions from an ether solution by sodium carbonate and by sodium hydroxide, giving a practically quantitative yield of benzoic acid (separated from V by extraction with hot water), 1.0 g. (79%) of VI, and a small amount of V.

2-Chloro-2,5-diphenyl-3-furanone (IX) was prepared by the action of benzoyl chloride containing a trace of concd. sulfuric acid on the enol. When shaken with cold sodium methylate solution for five minutes it is converted into III(B) in good yield. On standing for one hour in dilute methanolic sodium hydroxide solution, it is converted in good yield into the enol.

2-Benzoyloxy-2,5-diphenyl-3-furanone, X.—(a) Half a gram of IX with 2 g. of silver benzoate (freshly precipitated from alcoholic silver nitrate by means of sodium benzoate and washed with isopropyl ether) was suspended in 30 cc. of isopropyl ether and the mixture refluxed for ten hours. On filtering and working up the product 0.4 g. of nearly pure X was obtained.

(b) A mixture of 3 g. of enol, 9 g. of benzoic anhydride, and one drop of concd. sulfuric acid, was allowed to stand for one hour. The benzoic anhydride was decomposed with aqueous sodium bicarbonate solution. The residue on crystallization from isopropyl ether gave 2 g. of nearly pure X, m. p. 162–163° (corr.). *Anal.* Calcd. for $C_{23}H_{16}O_4$: C, 77.50; H, 4.53. Found: C, 77.49; H, 4.67.

The reactions outlined in the diagram were carried out in the usual way. The hydrolysis to the enol took place within a few minutes at room temperature.

2-Benzoyloxy-1,2-dibenzoylethylene (dibenzoylethenol benzoate), XII (or XIII), was prepared in yields of 50% or less by adding benzoyl chloride to a well-stirred suspension of the enol in an excess of aqueous sodium hydroxide solution. The product, obtained as an oil, was recrystallized from isopropyl ether or ethanol. The alkaline solutions always contained considerable enol which was recovered on acidification; m. p. 139° (corr.). *Anal.* Calcd. for $C_{23}H_{16}O_4$: C, 77.50; H, 4.53. Found: C, 77.30; H, 4.57.

The conversion to III(B) was accomplished by allowing the benzoate to stand for several hours in methanol saturated with hydrogen chloride. Both sodium hydroxide in 80% methanol and sodium methylate solution quickly hydrolyzed it to the enol. On standing for one-half to one hour in acetic anhydride or acetyl chloride containing a trace of concd. sulfuric acid, followed by hydrolysis and recrystallization, good yields of XIV (A) and (B), respectively, were obtained.

2-Hydroxy-2,5-diphenyl-4-methylfuranone, XV.—A mixture of 5 g. of the silver salt, 4 g. of methyl iodide and 35 cc. of isopropyl ether was refluxed for one hour. The solution was then filtered to remove silver halide, and extracted with 10% sodium hydroxide to remove the product, which is readily soluble in alkali. The alkaline solution was acidified and the crude product isolated by extraction with ether. The original isopropyl ether solution after the alkali extraction was evaporated and gave an oil from which 0.3 g. (about 10%) of dibenzoylmethoxyethylene was obtained. The carbon-alkyl product was purified by repeated crystallizations from isopropyl ether

and melted at 143–144° (corr.), yield 70%. *Anal.* Calcd. for $C_{17}H_{14}O_3$: C, 76.7; H, 5.30. Found: C, 76.6; H, 5.47.

The carbon-alkyl compound does not react with diazomethane under ordinary conditions and gives no color test with alcoholic ferric chloride, but reacts readily with bromine and dissolves easily and directly in dilute sodium hydroxide.

Hydrolytic fission was effected by steam distillation of a barium hydroxide solution. Propiophenone was isolated from the distillate and identified as the semicarbazone by mixed melting point with an authentic sample. The barium hydroxide solution on acidification and extraction with ether gave phenylglyoxylic acid (also identified as the semicarbazone).

$C_6H_5\overset{\text{O}}{\text{C}}(\text{OH})\text{COC}(C_2H_5)=CC_6H_5$, **2-Hydroxy-2,5-diphenyl-4-ethylfuranone**, was prepared and isolated in 50% yield by following the above procedure using ethyl iodide. The yield of dibenzoylthoxyethylene obtained as a by-product was 20%. The carbon-alkyl compound was purified by repeated crystallizations from isopropyl ether; m. p. 113° (corr.). It is soluble in dilute sodium hydroxide. *Anal.* Calcd. for $C_{15}H_{12}O_3$: C, 77.1; H, 5.76. Found: C, 76.9; H, 5.93. Hydrolytic fission with barium hydroxide, carried out as described above, gave phenylglyoxylic acid and phenyl propyl ketone which were identified as the semicarbazones.

$C_6H_5\overset{\text{O}}{\text{C}}(\text{OH})\text{COC}(C_3H_7)=CC_6H_5$, **2-Hydroxy-2,5-diphenyl-4-propylfuranone**, was prepared as above using *n*-propyl iodide (yield 45%). From the non-acidic oily residues no crystalline *o*-alkyl product was obtained. The product was purified by repeated crystallization from isopropyl ether; m. p. 137.5° (corr.). It is soluble in sodium hydroxide. *Anal.* Calcd. for $C_{16}H_{14}O_3$: C, 77.5; H, 6.17. Found: C, 77.3; H, 6.20.

Hydrolytic fission carried out as above gave phenylglyoxylic acid and phenyl *n*-butyl ketone, identified as semicarbazones.

Summary

New studies including the application of the quinoxaline reaction have been made on 1,4-diphenyl-1,2,4-butanetrione enol and derivatives. These studies, together with reconsideration of known facts, show that the methyl ether obtained from the enol by catalytic etherification, and the chloro compound obtained by the action of thionyl chloride, have cyclic formulas.

The benzoylation of the enol under different conditions gives a cyclic oxygen-benzoyl compound, an open chain enol benzoate, and a carbon-benzoyl derivative.

Evidence is given for the simultaneous formation in considerable amounts of the true structurally isomeric enol ether, diphenyl-4-methoxy-1,2-butenedione in the methylation of the enol with diazomethane.

The bearing of the new facts on the structure of the two forms of the enol is discussed.

Alkylation of the silver salt leads to a mixture of oxygen and carbon-alkyl compounds, the latter type predominating.

The analogy between the enol and hydroxynaphthoquinone is discussed.

UNIVERSITY, VA.

RECEIVED MAY 8, 1936

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

The Mechanism of Carbohydrate Oxidation. XXI.¹ The Synthesis of Glucosidoglyceraldehyde Derivatives

BY HAROLD W. ARNOLD AND WILLIAM LLOYD EVANS

In interpreting the results of the alkaline degradation of gentiobiose (6-glucosidoglucose), Evans and Hockett² postulated the intermediate formation of 3-glucosidoglyceraldehyde as the result of the fragmentation of the gentiobiose in an alkaline solution. It was with the ultimate purpose of testing this hypothesis that the synthesis of 3-glucosidoglyceraldehyde derivatives was undertaken.

The synthesis involved the condensation of acetobromo-*d*-glucose with glyceraldehyde ben-

zyl-cyclo-acetal³ (a compound of the type known to have an unblocked hydroxyl group on the third carbon atom) according to the procedure of Königs and Knorr⁴ as improved by Kreider and Evans^{1,5} with the formation of crystalline 3- β -*d*-glucosido-glyceraldehyde benzyl-cyclo-acetal tetraacetate (I). In order to test the applicability of Hudson's rules of isorotation to disaccharide derivatives containing the glyceraldehyde benzyl-cyclo-acetal residue, 3- β -*l*-arabinosidoglyceraldehyde benzyl-cyclo-acetal triacetate (II) was like-

(1) No. XX of this Series, *THIS JOURNAL*, **58**, 1661 (1936).

(2) W. L. Evans and R. C. Hockett, *THIS JOURNAL*, **53**, 4384 (1931).

(3) H. O. L. Fischer and Erich Baer, *Ber.*, **65**, 337 (1932).

(4) W. Königs and E. Knorr, *ibid.*, **34**, 957 (1901).

(5) L. C. Kreider and W. L. Evans, *THIS JOURNAL*, **57**, 229 (1935).