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).

$C_6H_5\overset{\text{O}}{\overbrace{C(OH)COC(C_2H_5)=C}}C_6H_5$, **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 dibenzoylethoxyethylene 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 $C_{18}H_{16}O_3$: 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.

$C_6H_5\overset{\text{O}}{\overbrace{C(OH)COC(C_3H_7)=C}}C_6H_5$, **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 $C_{19}H_{18}O_3$: 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 Hockett[2] 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 benzyl-cyclo-acetal[3] (a compound of the type known to have an unblocked hydroxyl group on the third carbon atom) according to the procedure of Königs and Knorr[4] 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).

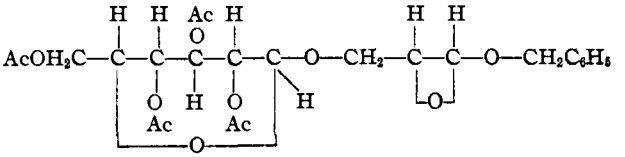
wise prepared by the condensation of acetobromo-*l*-arabinose with glyceraldehyde benzyl-cyclo-acetal.

Upon hydrogenation in the presence of palladium black, (I) yielded amorphous 3-*β*-*d*-glucosidoglyceraldehyde tetraacetate (III). The complete cleavage of glyceraldehyde benzyl-cyclo-acetal acetate and related compounds had already been demonstrated by Fischer and Baer.[3] More thorough studies by Richtmyer[6] had shown that only benzyl glycosides are completely split by catalytic hydrogenation.

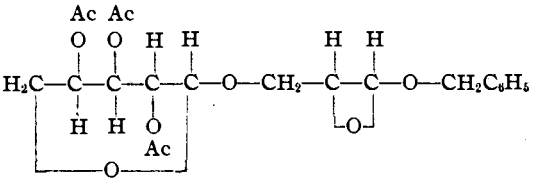
Refluxing of (III) with anhydrous pyridine, followed by acetylation, yielded a sirup which reacted with *p*-nitrophenylhydrazine to form the crystalline *p*-nitrophenylhydrazone of *β*-*d*-glucosidodihydroxyacetone pentaacetate.[5] The yield of this hydrazone indicated an 8–9% conversion of the glucosidoglyceraldehyde derivative to the corresponding glucosidodihydroxyacetone derivative. Fischer, Taube and Baer,[7] in similar studies of the action of pyridine on glyceraldehyde, found a maximum conversion to dihydroxyacetone of 49%.

In the course of experiments carried out in the attempt to improve the yield of glyceraldehyde benzyl-cyclo-acetal from glyceraldehyde, it was found that glyceraldehyde diacetate on treatment with titanium tetrachloride according to the method of Pacsu,[8] smoothly yielded acetochloroglyceraldehyde. This underwent the Königs–Knorr[4] reaction with benzyl alcohol to form what was apparently a mixture of isomeric benzyl glycoside acetates. From the mixture it was possible to separate the benzyl-cyclo-acetal acetate described by Fischer and Baer.[3]

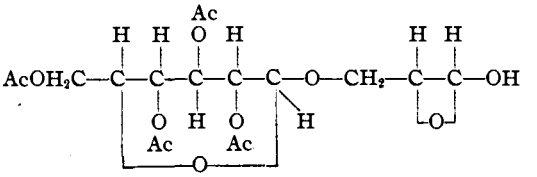
In formulating the compounds shown, the ethylene oxide formula has been ascribed to the glyceraldehyde residues. This has been done to conserve space and is not meant to imply that the glyceraldehyde derivatives described have this structure. Although many of the properties of dimeric glyceraldehyde and its simple derivatives can be accounted for on the basis of an associated ethylene oxide formula, more recent work[9] points to a dioxane ring structure for dimeric glyceraldehyde and its derivatives. The *β*-*d*-glucosidoglyceraldehyde benzyl-cyclo-acetal tetraacetate described in this paper appears to be almost entirely dimeric in benzene at the freezing point and almost wholly monomeric at the temperature of melted camphor.



(I) 3-*β*-*d*-Glucosidoglyceraldehyde benzyl-cyclo-acetal tetraacetate



(II) 3-*β*-*l*-Arabinosidoglyceraldehyde benzyl cyclo-acetal triacetate



(III) 3-*β*-Glucosidoglyceraldehyde-tetraacetate

The results obtained in the study of the alkaline degradation of glucosidoglyceraldehyde tetraacetate will be incorporated into a later paper.

Experimental Part

Preparation of Reagents and Starting Materials.—The crystallineglyceraldehyde used in this work was obtained from the laboratory of Dr. Fraenkel and Dr. Landau, Berlin-Oberschöneweide. It melted at 141°.

The acetobromo-*d*-glucose was prepared according to the procedure of Freudenberg.[10] It was recrystallized twice from anhydrous ether and extensively dried *in vacuo*.

The acetobromo-*l*-arabinose was prepared as described by Hudson and Dale.[11] It was purified as described above.

The glyceraldehyde benzyl-cyclo-acetal was prepared, with a few minor modifications, according to the method of Fischer and Baer.[3] The pyridine used was purified by refluxing and fractionating over barium oxide.

Other materials were prepared and purified as described by Kreider and Evans.[12]

3-β-d-Glucosidoglyceraldehyde Benzyl-cyclo-acetal Tetraacetate.—The preparation of this compound was carried out in a three-necked flask fitted with a powerful mercury-sealed stirrer. One neck of the flask carried a

(6) N. K. Richtmyer, THIS JOURNAL, **56**, 1633 (1934).

(7) H. O. L. Fischer, Carl Taube and Erich Baer, *Ber.*, **60**, 479 (1927).

(8) Eugen Pacsu, *ibid.*, **61**, 1510 (1928); THIS JOURNAL, **52**, 2563 (1930).

(9) H. G. Reeves, *J. Chem. Soc.*, 2477 (1927); M. Bergmann, A. Miekley and E. von Lippmann, *Ber.*, **62**, 1467 (1929); M. Bergmann and A. Miekley, *ibid.*, **62**, 2297 (1929); W. Discherl and E. Braun, *ibid.*, **63**, 416 (1930).

(10) K. Freudenberg, A. Noë and E. Knopf, *ibid.*, **60**, 241 (1927).

(11) C. S. Hudson and J. K. Dale, THIS JOURNAL, **40**, 992 (1918); *cf.* P. A. Levene and A. L. Raymond, *J. Biol. Chem.*, **90**, 247 (1931).

(12) L. C. Kreider and W. L. Evans, THIS JOURNAL, **58**, 797 (1936).

dropping funnel, the other a calcium chloride tube. The following mixture was introduced into the flask and rapidly stirred for thirty minutes: 11.0 g. of glyceraldehyde benzyl-cyclo-acetal (1 mol), 22.0 g. of silver carbonate, 50.0 g. of finely powdered "Drierite," and 120 cc. of benzene. A solution of 25.1 g. (1 mol) of acetobromo-*d*-glucose in 110 cc. of benzene was then slowly added through the dropping funnel, the initial rate of addition being somewhat faster than at the end. The addition required approximately thirty minutes. As the addition progressed there was a rapid evolution of carbon dioxide, a marked rise in temperature (10°), and a noticeable change in color. The mixture was stirred for at least five hours after the addition of the acetobromoglucose was complete. It was then filtered by suction and the residue repeatedly washed with small quantities of benzene. The benzene solution was then evaporated to dryness *in vacuo* at room temperature. The half crystalline residue was dissolved in the least possible volume of boiling ethyl alcohol. When allowed to cool the product precipitated in clumps of needles. After three recrystallizations from ethyl alcohol and two from methyl alcohol the melting point was constant at 172–173° (corr.). The weight of crystals (needles) was 15.5 g., corresponding to a yield of 50%, calculated on the basis of the acetobromoglucose used; $[\alpha]^{23}D$ −19.9° (*c*, 1.7; $CHCl_3$).

Anal. Calcd. for $C_{16}H_{18}O_8(COCH_3)_4$: acetyl, 7.83 cc. of 0.1 *N* NaOH per 100 mg. Found: acetyl, 7.79 cc., 7.80 cc. *Mol. wt.* Calcd. for $(C_{24}H_{30}O_{12})_2$: 1020. Found: (cryoscopic in benzene) 995. Calcd. for $C_{24}H_{30}O_{12}$: 510. Found: (Rast) 562.

The compound is readily soluble in ether, chloroform, benzene, ethyl acetate and acetone. It is insoluble in water and petroleum ether, and only slightly soluble in cold methyl or ethyl alcohol. The substance reduces hot Fehling's solution only after hydrolysis by dilute mineral acid.

3-β-*l*-Arabinosidoglyceraldehyde Benzyl-cyclo-acetal Triacetate.—The procedure which was followed in preparing this compound was exactly the same as that described under the preparation of the corresponding β-*d*-glucosido derivative. The following quantities of reactants were used: glyceraldehyde benzyl-cyclo-acetal, 3.06 g. (1 mol); silver carbonate, 9.88 g.; "Drierite," 20.0 g.; acetobromo-*l*-arabinose, 5.8 g. (1 mol); benzene, 150 cc. The product was crystallized to constant melting point and rotation from methyl alcohol. The weight of the pure product (needles) was 0.51 g., corresponding to a yield of 7%, calculated on the basis of the acetobromoarabinose used; m. p. 142–143° (corr.) $[\alpha]^{22}D$ +4.2° (*c*, 1.2; $CHCl_3$).

Anal. Calcd. for $C_{15}H_{17}O_7(COCH_3)_4$: acetyl, 6.84 cc. of 0.1 *N* NaOH per 100 mg. Found: acetyl, 6.78 cc.

3-β-*d*-Glucosidoglyceraldehyde Tetraacetate.—Because of the danger of hydrolysis of the glycosidic link in acid media, the cleavage of β-*d*-glucosidoglyceraldehyde benzyl-cyclo-acetal tetraacetate was carried out in purified methyl alcohol. The palladium catalyst was prepared according to the method of Tausz and von Putnoky.[13] The apparatus used was a modification of that described by Gattermann-Wieland.[14] The following procedure was followed in carrying out the hydrogenations. The catalyst and the solvent were introduced into the hydrogenation flask and rapidly shaken in a hydrogen atmosphere until absorption of hydrogen ceased. The sample was then introduced and the system flooded with hydrogen. The flask was again shaken until absorption of hydrogen ceased. At the beginning practically none of the substance was in solution, whereas, when hydrogen absorption was complete, the solution was homogeneous. At the end of a run the odor of toluene was very marked. The solution was filtered rapidly through a porous-bottomed crucible, care being taken to prevent contact of the catalyst with the air because of the danger of igniting the solvent vapors.

The results of two typical hydrogenations are tabulated below.

Wt. of compound, g.	3.21	4.00
Wt. of catalyst, g.	1.00	1.00
Vol. of CH_3OH, cc.	100	100
Vol. of H_2 absorbed (std. concns.), cc.	158	291
Theoretical vol. of H_2 (1 mol), cc.	144	176
Theoretical wt. of debenzylated compound, g.	2.70	3.30
Actual wt. of reaction product, g.	2.68	3.27

After removal of the catalyst by filtration, the filtrate and washings were evaporated *in vacuo* to about one-fourth their volume. The remaining solution was decolorized with Norite, chilled in ice for several hours, and filtered. The filter and all other vessels used were washed out repeatedly with methyl alcohol to ensure complete transference of the product. The solution was evaporated in a crystallizing dish to a thick, colorless sirup in a vacuum desiccator. This was redissolved in a small volume of chloroform and the solution again evaporated to dryness. The same treatment was repeated successively with pure chloroform, 50% chloroform and petroleum ether (30–60°), 20% chloroform in petroleum ether, and three times with petroleum ether. The dish was covered with a watch glass during these operations to prevent loss by spattering. After the foregoing treatment, the product could be powdered. Microscopic examination showed it to be amorphous. All attempts to bring about crystallization from a large number of solvents and combinations of solvents have failed up to the present.

Anal. Calcd. for $C_9H_{12}O_8(COCH_3)_4$: acetyl, 9.52 cc. of 0.1 *N* NaOH per 100 mg. Found: acetyl, 9.65 cc., 9.57 cc. *Mol. wt.* Calcd. for $(C_{17}H_{24}O_{12})_2$: 850. Found: (cryoscopic in benzene) 840.

The amorphous solid melts to a thick sirup at 63°. Since this amorphous substance was analytically pure, a determination of the specific rotation was thought to be of value. The following result was obtained: $[\alpha]^{24}D$ −15.5° (*c*, 1.8; $CHCl_3$). Attempts to prepare crystalline derivatives by acetylation and benzoylation failed. Likewise did the attempts to prepare substituted phenylhydrazones. The substance rapidly reduces Fehling's solution in the cold.

Conversion of β-*d*-Glucosidoglyceraldehyde Tetraacetate to β-*d*-Glucosidodihydroxyacetone Pentaacetate.—The record of two experiments is given below. The

(13) J. Tausz and N. von Putnoky, *Ber.*, **52B**, 1573 (1919).

(14) L. Gattermann and H. Wieland, "Laboratory Methods of Organic Chemistry," The Macmillan Co., New York, 1932, p. 367.

glucosidoglyceraldehyde tetraacetate was refluxed with anhydrous pyridine (drying tube) at a bath temperature of 135–140°. The solution was then cooled somewhat and 10 cc. of acetic anhydride was added. The mixture was then allowed to stand overnight. It was poured into 500 cc. of ice water which was then extracted with 200 cc. of chloroform in small portions. The chloroform solution was washed successively with dilute sulfuric acid, sodium bicarbonate solution and water. It was dried over calcium chloride. Removal of the chloroform left a thick sirup which could not be crystallized. It was taken up in ethyl alcohol and heated on the water-bath with a saturated ethyl alcohol solution of *p*-nitrophenylhydrazine. The solution was then allowed to concentrate spontaneously over a period of a week. At the end of this time, reddish-yellow crystals had separated out. These were recrystallized three times from 95% ethyl alcohol, giving pale yellow needles which melted at 187° (corr.). Mixed melting point with an authentic sample of the *p*-nitrophenylhydrazone of *β*-*d*-glucosidodihydroxyacetone pentaacetate was likewise 187°; $[\alpha]^{23}D$ −126.5°. In calculating the per cent. conversion, the reaction between the dihydroxyacetone derivative and *p*-nitrophenylhydrazine is assumed to be complete. Experimental losses are also neglected.

Wt. of glucosidoglyceraldehyde tetraacetate, g.	1.5	1.5
Vol. of pyridine, cc.	15	15
Time of refluxing, hrs.	2	3.5
Wt. of pure *p*-nitrophenylhydrazone, g.	0.18	0.20
Per cent. conversion	8.4	9.4

Acetochloroglyceraldehyde.—The results of a series of experiments on the action of titanium tetrachloride on dimeric glyceraldehyde diacetate are given below in tabular form.

The glyceraldehyde diacetate was dissolved in purified chloroform. A 10% solution of purified titanium tetrachloride in anhydrous, alcohol-free chloroform was rapidly added and the mixture protected from moisture by a drying tube. Immediately after mixing a lemon-colored addition compound precipitated out. The mixture was then refluxed on the water-bath or allowed to stand at room temperature. The precipitated solid gradually became darker in color, being almost black at the end of the reaction. The mixture was poured into a large volume of ice water. The chloroform layer was separated and the water layer repeatedly extracted with small portions of chloroform until the volume of chloroform solution amounted to 200 cc. per gram of diacetate used. The chloroform layer was washed several times with water and then with sodium carbonate solution. It was dried over calcium chloride. Evaporation of the chloroform under reduced pressure left a light brown-colored residue which was recrystallized by dissolving in the least possible quantity of boiling chloroform. When the solution had reached room temperature, an equal volume of petroleum ether (30–60°) was added and the mixture cooled in ice for several hours.

The pure compound crystallized in fine needles. It was insoluble in water and petroleum ether, sparingly soluble in chloroform, ether, and benzene at ordinary temperatures, and easily soluble in acetone.

SUMMARY OF RESULTS

Diacetate, g.	$TiCl_4$, g.	Time of refluxing, hours	Yield, %
1.0	1.0	4	49.7
4.0	4.0	4	35.0
4.5	4.8	6	15.4
1.0	1.0	14—rm. temp.	87.0
1.0	1.0	18—rm. temp.	83.3
1.0	1.0	23—rm. temp.	81.0

M. p. 174–175° (corr.). *Anal.* Calcd. for $C_5H_7O_3Cl$: Cl, 23.56. Found: Cl, 23.52.

Reaction of Acetochloroglyceraldehyde with Benzyl Alcohol.—A mixture of 2.1 g. of acetochloroglyceraldehyde, 6 g. of silver carbonate and 30 cc. of benzyl alcohol was shaken for eighteen hours at room temperature. At the end of this time it was heated on the water-bath for one hour. Following this it was cooled in ice for several hours before filtering. The residue was dried as far as possible by suction filtration, being washed with a little ice-cold ethyl alcohol to remove excess benzyl alcohol. It was then repeatedly extracted with boiling ethyl alcohol and finally with boiling chloroform, the alcohol and chloroform extracts being combined. The solvents were removed by a warm air stream, and the residual crystals recrystallized from the least possible volume of boiling 50% alcohol. The weight of crystals after the first recrystallization was 2.3 g. The melting range was very wide. Melting began at 110° and was complete at 135°. After five recrystallizations from the same solvent, the weight of the substance was 0.75 g. and the melting point was constant at 141–142° (corr.). A mixed melting point with glyceraldehyde benzyl-cyclo-acetal acetate, prepared according to the procedure of Fischer and Baer,[3] showed no depression.

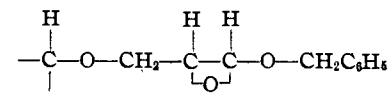
Anal. Calcd. for $C_{10}H_{11}O_3COCH_3$: acetyl, 4.50 cc. of 0.1 *N* NaOH per 100 mg. Found: acetyl (for substance melting at 110–135°), 4.44 cc.; (for substance melting at 141–142°) 4.45 cc.

By appropriate procedures it was possible to isolate from the mother liquors a small quantity of crystals melting at 109–110° (corr.). The quantity was not large enough for further work.

The results seem to point to the presence of two isomeric benzyl-cyclo-acetal acetates.

Discussion

In a manner similar to that suggested by Kreider and Evans[12] the rotations of *β*-*d*-glucosidoglyceraldehyde benzyl-cyclo-acetal tetraacetate and *β*-*l*-arabinosidoglyceraldehyde benzyl-cyclo-acetal triacetate may be considered in accordance with Hudson's views to be the sum of two components, A and B, A being used to designate that part of the rotation due to the group



and B that due to the remainder of the molecule. Since *l*-arabinose has been shown by Isbell[15] to be

(15) H. S. Isbell, *J. Chem. Ed.*, **12**, 96 (1935).

genetically related to *d*-glucose, the A values for the *d*-glucosido derivative and the *l*-arabinosido derivative should have the same sign. If the principle of optical superposition is valid, the A values should also have approximately the same magnitude. The B values for the two derivatives may be calculated from the rotations of the α- and β-forms of the fully acetylated parent sugars. The A values may then be calculated from the experimentally determined rotations of the two glycosido derivatives. The values for the molecular rotation of A as calculated by this method are: β-*d*-glucosidoglyceraldehyde benzyl-cyclo-acetal tetraacetate, A −30,500; β-*l*-arabinosidoglyceraldehyde benzyl-cyclo-acetal triacetate, A −31,990. The difference between the numerical values of Hudson's A for the two derivatives is very nearly equal to that reported by Kreider and Evans[12] for the corresponding dihydroxyacetone derivatives.

Summary

1. β-*d*-Glucosidoglyceraldehyde benzylcyclo-acetal tetraacetate and β-*l*-arabinosidoglyceraldehyde benzyl-cyclo-acetal triacetate have been prepared in crystalline condition.

2. Cleavage of β-*d*-glucosidoglyceraldehyde benzyl-cyclo-acetal tetraacetate by catalytic hydrogenation yields β-*d*-glucosidoglyceraldehyde tetraacetate as an amorphous solid with an acetyl number and a molecular weight in good accord with the theory.

3. Refluxing β-*d*-glucosidoglyceraldehyde tetraacetate in anhydrous pyridine, followed by acetylation, gives β-*d*-glucosidodihydroxyacetone pentaacetate in yields of 8–9%, based on the quantities of the *p*-nitrophenylhydrazone of the latter compound isolated.

4. Acetochloroglyceraldehyde has been prepared in the crystalline condition. This reacts with benzyl alcohol to yield what is apparently a mixture of isomeric glyceraldehyde benzyl-cyclo-acetal acetates.

COLUMBUS, OHIO RECEIVED JULY 11, 1936

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HOWARD UNIVERSITY]

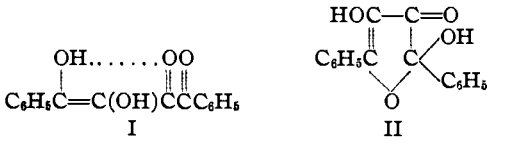
Hydroxy Polyketones. III.[1] Benzoylformoin

BY A. H. BLATT

In an earlier article[2] we described the alkylation of benzoylformoin and presented the evidence for a revision of the structures formerly assigned to its alkylation products. In this article we complete our description of the chemical behavior of the formoin and its derivatives.

The chemistry of benzoylformoin is that of a tautomeric mixture of the ene-diol (I) and the dihydroxyfuranone (II). While certain of its reactions may be ascribed to the alternative ene-diol (III) and to the hydroxy ketone (IV), there are no reactions of the material which require the existence of these latter two forms and the entire behavior of the formoin can be accounted for on the basis of an equilibrium between (I) and (II). The reactions which form the basis for these conclusions will now be described.

Salt formation, oxidation and quinoxaline formation characterize benzoylformoin as an ene-diol. Werner described, without analytical data, a series of lakes obtained from the formoin and salts of several heavy metals.[3] Sidgwick[4] considers that these salts are derived from the completely chelated ene-diol (III) and that they contain two five-membered chelate rings. In the absence of all details as to the composition of the salts this conclusion seems to us to be somewhat hazardous. We have succeeded in securing a copper derivative of the formoin which is obviously derived from an ene-diol for its composition corresponds to the replacement of two atoms of hydrogen by one of copper. However,



$C_6H_5COC(OH)=C(OH)COC_6H_5$ (III)

$C_6H_5COCHOHCOCOC_6H_5$ (IV) $\qquad$ $C_6H_5COCOCOCOC_6H_5$ (V)

(1) Second paper, THIS JOURNAL, **58**, 81 (1936). Shortly after the present article was submitted to the Journal a paper by Karrer and Litwan appeared [*Helv. Chim. Acta*, **19**, 829 (1936)] in which conclusions similar to ours about the structure of the formoins are advanced on the basis of iodine titrations.

(2) Blatt, THIS JOURNAL, **57**, 1103 (1935).

(3) Werner, *Ber.*, **41**, 1070 (1908).

(4) Sidgwick, "Electronic Theory of Valence," Oxford University Press, Oxford, England, 1932, p. 245.