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]

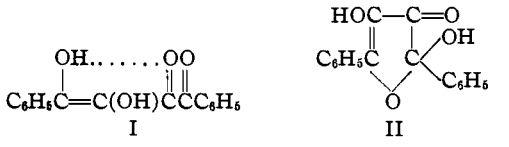
Hydroxy Polyketones. III.[1] Benzoylformoin

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,



I II

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

III

$C_6H_5COCHOHCOCOC_6H_5$ IV

$C_6H_5COCOCOCOC_6H_5$ 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).

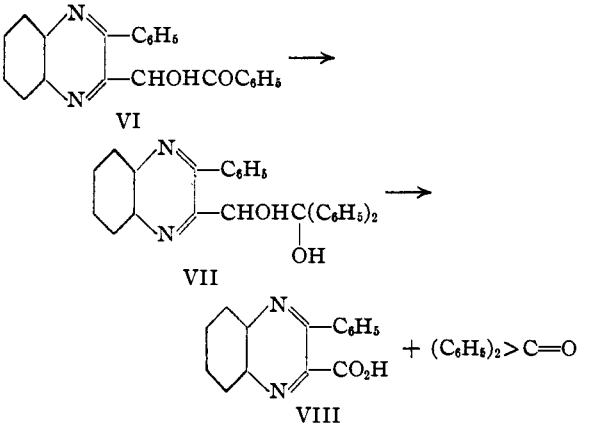
(4) Sidgwick, "Electronic Theory of Valence," Oxford University Press, Oxford, England, 1932, p. 245.

no indication as to which of the two possible ene-diols is involved in the salt formation is available from the metallic derivatives of the formoin.

The ease of oxidation of benzoylformoin is in agreement with its formulation as an ene-diol. The earliest work with the formoin showed that it was oxidized to diphenyl tetraketone (V) by nitric acid and by bromine.[5] It is also oxidized to the tetraketone by thionyl chloride. Quite recently, Karrer[6] has shown that the formoin is oxidized by iodine in acid solution and from the results of iodine titrations has concluded that it exists in solution to the extent of 57% as an ene-diol. We have not succeeded in isolating the tautomeric modifications whose existence is indicated by these titrations but we have found that the stable yellow crystalline formoin when vacuum distilled furnishes a deep red unstable liquid distillate which gradually reverts to the stable yellow modification. Since the color of the distillate is so similar to that of the alkaline solutions of benzoylformoin and to that of the unstable material which is first obtained on acidification of these alkaline solutions, we are of the opinion that the liquid is the ene-diol while the stable crystalline form is the dihydroxyfuranone. It is because of the greater volatility of the unstable modification that we have suggested the hydrogen bond (chelate linkage) shown in formula I.

Benzoylformoin is also oxidized by copper acetate in aqueous acetic acid.[6] Since we had found that the closely related dibenzoylcarbinol on oxidation with copper acetate furnishes benzil instead of diphenyl triketone,[1] we sought the oxidation product of the formoin with this reagent. The product is benzil. Diphenyl tetraketone likewise furnishes benzil on oxidation with copper acetate, as does benzoin. From these results it is evident that not only are α-hydroxy ketones oxidized by copper acetate in an acid medium but also that the oxidative elimination of carbonyl groups from linear tri- and tetraketones is a general reaction. We have confirmed this by oxidizing 2,4,6-trimethylbenzoylformoin and find that the process is completely analogous and furnishes dimesityl diketone.

With *o*-phenylenediamine, benzoylformoin furnishes the quinoxaline (VI) whose structure was established by the following sequence of reactions.



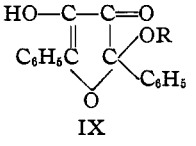
VI

VII

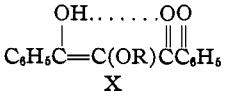
VIII

Quinoxaline formation may be ascribed to the hydroxy ketone tautomer (IV). We believe it is more reasonably considered as a reaction of the ene-diol (I) followed by ketonization and in a later paragraph we shall show that enolization of the hydroxy ketone system even in the quinoxaline (VI) can be brought about with surprising ease.

Alkylation and acylation of the formoin are predominantly the reactions of the furanone (II) but the course of these reactions can be directed by controlling the acidity or alkalinity of the reaction medium. Thus, alkylation with an alcohol and acid leads, as was shown earlier,[2] to cyclic derivatives such as (IX). Alkylation with methyl sulfate in sodium hydroxide solution, however, furnishes the open-chain ether (X, R = CH_3).



IX



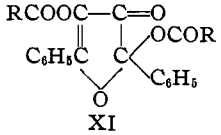
X

Acetylation leads to three acetyl derivatives: a diacetate and two isomeric monoacetates. Acetic anhydride alone or containing sulfuric acid, acetyl chloride alone or in pyridine, all furnish the cyclic diacetate (XI, R = CH_3). The two acetyl groups in this substance are easily hydrolyzed either by acids or bases.[5] Treatment with *o*-phenylenediamine effects partial hydrolysis removing the enolic ester group to furnish the monoacetate (XII). That it is the enolic ester group which is eliminated is shown by the fact that the acetate (XIII) on treatment with *o*-phenylenediamine undergoes a parallel reaction to furnish the methoxyl compound (IX, R = CH_3). With acetic anhydride and sodium hydroxide the formoin yields an isomeric monoacetate (XIV).

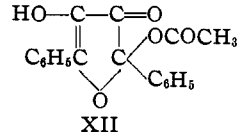
(5) Abenius, (a) *Bihang Till K. Sv. Vet.-Akad. Handl.*, **20**, 3 (1894); (b) *Ber.*, **27**, 706 (1894).

(6) Karrer and v. Segesser, *Helv. Chim. Acta*, **18**, 273 (1935); Karrer and Musante, *ibid.*, p. 1140.

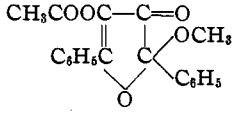
This monoacetate, like its isomer, may be hydrolyzed by acids or bases and with acetic anhydride and sulfuric acid forms the cyclic diacetate (XI). With *o*-phenylenediamine the monoacetate (XIV) furnishes the hydroxyquinoxaline (XV).



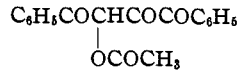
XI



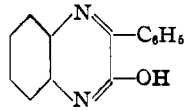
XII



XIII

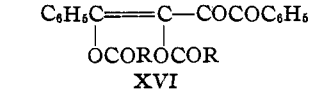


XIV

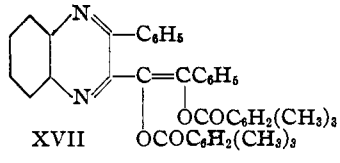


XV

The acetyl derivatives of the formoin are so readily hydrolyzed that it is difficult to secure reliable information about them. In order to get around this difficulty, we treated benzoylformoin with 2,4,6-trimethylbenzoyl chloride, expecting that the resulting highly substituted acyl derivative would be relatively insensitive. This proved to be the case and we obtained a diacyl derivative of the ene-diol having the structure (XVI, R = 2,4,6-$(CH_3)_3C_6H_2$—) for it reacted with *o*-phenylenediamine to form the quinoxaline (XVII) which could be oxidized to the known hydroxyquinoxaline (XV). It is not improbable that acetylation with acetyl chloride in pyridine, which eventually leads to the diacetate (XI, R = CH_3), furnishes first a diacetate (XVI, R = CH_3) which is rearranged by acids to the product actually obtained, for the diacyl derivative (XVI, R = 2,4,6-$(CH_3)_3C_6H_2$—) is converted by prolonged treatment with acid to an isomer which does not react with *o*-phenylenediamine. The di-(trimethyl)-benzoate (XVI) in which no mobile hydrogen atom is present is the only derivative of the ene-diol to which a structure free from ambiguity can be ascribed.

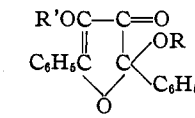


XVI

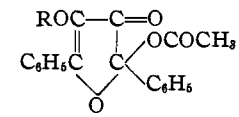


XVII

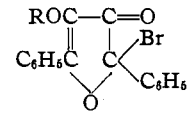
Considering next the dialkyl derivatives of benzoylformoin which have the structure (XVIII), we find that the glycosidic alkyl group is distinguished from the enolic alkyl group by its behavior toward acetic anhydride and sulfuric acid and toward hydrogen bromide in acetic acid. With the former reagent alkoxyl is replaced by acetoxyl to furnish the alkoxy acetate (XIX), isomeric with the previously mentioned acetate (XIII) and differing from it in that it is unaffected by *o*-phenylenediamine. With hydrogen bromide both the dialkyl derivatives (XVIII) and the alkoxy acetates (XIX) yield the bromofuranone (XX). The bromofuranone was not isolated in a pure state because it was always accompanied by the dimolecular product (XXI). The ease of formation of dimolecular products is even more pronounced in the case of our bromofuranones than with the analogous triphenylbromofuranone recently described by Kohler.[7] Our bromofuranones (XX) are converted to the dimolecular compounds by prolonged treatment with hydrogen bromide in acetic acid—a fact of particular interest in connection with recent observations on the reduction of α-bromo ketones by hydrogen bromide.[8]



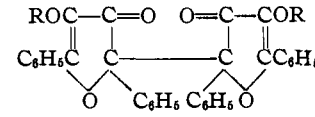
XVIII



XIX



XX



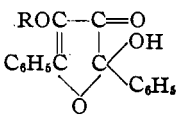
XXI

The open chain monomethyl derivative of benzoylformoin, like benzoylformoin, shows the behavior of a tautomeric mixture of the two forms: (X, R = CH_3) and (XXII, R = CH_3). With *o*-phenylenediamine it furnishes the quinoxaline (XXIII), on acid methylation the dialkyl derivative (XVIII, R, R′ = CH_3), on acetylation the acetate (XIX, R = CH_3) and with hydrogen bromide the dimolecular product (XXI, R = CH_3). The ordinary crystalline pale yellow monomethyl derivative is probably the furanone (XXII, R = CH_3). On distillation it furnishes a red modification, presumably (X, R = CH_3), whose color is analogous to that of the alkaline

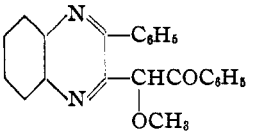
(7) Kohler, Westheimer and Tishler, THIS JOURNAL, **58**, 264 (1936).

(8) Kröhnke and Timmler, *Ber.*, **69**, 614 (1936).

solutions of the ether and to the color of the first unstable product obtained by acidifying these alkaline solutions.

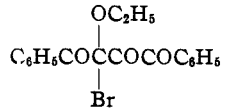


XXII

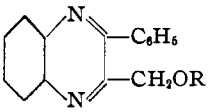


XXIII

The facts presented up to this point furnish a consistent picture of benzoylformoin and its open chain monoalkyl derivatives as ene-diol—hydroxyfuranone tautomers, and of its cyclic mono- and di-alkyl derivatives as alkoxyfuranones. There are two facts, however, which, while they are no better interpreted on any alternative formulation, are less concordant. The first is the stability of the formoin and its open chain monoalkyl derivatives toward alkali. While they are cleaved, as one would expect of α-diketones, by alkaline peroxide, they do not undergo a benzilic acid rearrangement with alkali alone. The second is the behavior of the open chain monoethyl derivative (X, R = C_2H_5, and XXII, R = C_2H_5). On acid alkylation, with hydrogen bromide, and with acetic anhydride and sulfuric acid it behaves like its methyl analog. With *o*-phenylenediamine, however, it does not give a quinoxaline analogous to (XXIII) but, instead, like the acetate (XIV) furnishes the hydroxyquinoxaline (XV). With bromine it yields a monobromo derivative for which no other structure than (XXIV) is reasonable but which is remarkably stable for a substance having such a structure.



XXIV



XXV

Finally attention should be called to the behavior of the quinoxalines (VI) and (XXIII) toward sodium methylate. On treatment with this reagent they form intensely colored solutions reminiscent of those of the metallic derivatives of stilbene diol. These solutions gradually lose their color and furnish methyl benzoate, benzoic acid, the hydroxyquinoxaline (XV) and from the quinoxaline (VI) the carbinol (XXV, R = H), from the quinoxaline (XXIII) the ether (XXV, R = CH_3). The formation of methyl benzoate, the carbinol (XXV, R = H) and its methyl ether (XXV, R = CH_3) are obviously due to the addition of alcohol or alcoholate and subsequent cleavage—a process similar to the alcoholysis of dibenzoylcarbinol.[1] The formation of the hydroxyquinoxaline (XV) must be a result of an oxidation process.

Experimental

Benzoylformoin distils at about 240° at a pressure of 0.5 mm. The deep red distillate on standing or on solution in alcohol reverts to the ordinary yellow stable crystalline form. Our previous statement[2] that the formoin decomposed on melting is incorrect. The formoin undergoes gradual autoxidation on standing.

Salt Formation and Oxidation.—In ethereal solution shaken with copper acetate benzoylformoin furnishes a brown copper derivative of the ene-diol. For analysis the copper derivative was washed with ether and vacuum dried.

Anal. Calcd. for $C_{16}H_{10}O_4Cu$: Cu, 19.23. Found: Cu, 18.84.

When benzoylformoin was boiled with thionyl chloride a carmine red solution resulted. Evaporation of this solution over alkali in a desiccator left diphenyl tetraketone (V). The tetraketone crystallized from benzene in splendid scarlet crystals melting at 110–112° and was identified by a mixed melting point with a synthetic sample prepared by the nitric acid oxidation of benzoylformoin.[9] The product of the nitric acid oxidation is the tetraketone hydrate which is easily converted to the anhydrous material by high vacuum distillation.

When benzoylformoin was dissolved in 60% acetic acid and warmed at 80° for one hour with an excess of saturated aqueous copper acetate, then filtered hot from the precipitated cuprous oxide and diluted with water, an excellent yield of benzil was obtained. On similar treatment diphenyl tetraketone and benzoin also gave benzil.

When 2,4,6-trimethylbenzoylformoin[10] was oxidized in the same way with copper acetate the product melted at 117–118°. Since the melting point did not suffice to distinguish between the two possible products, dimesityl triketone[11] and dimesityl diketone,[12] the product was analyzed and found to be the diketone. (*Anal.* Calcd. for $C_{20}H_{22}O_2$: C, 81.6; H, 7.5. Found: C, 81.6; H, 7.67.) The yield is excellent and the process makes readily available this highly hindered diketone.

Quinoxaline Formation.—When 5.4 g. of benzoylformoin dissolved in 30 cc. of hot methanol was boiled for one hour with an excess (3.0 g.) of *o*-phenylenediamine, the solution on cooling deposited 4.7 g. of the quinoxaline (VI). For analysis the material was crystallized from acetic acid. It was sparingly soluble in the ordinary solvents and melted to a red liquid at 187–188°.

Anal. Calcd. for $C_{22}H_{16}O_2N_2$: C, 77.6; H, 4.7. Found: C, 77.36; H, 4.7.

To establish the structure of the quinoxaline (VI) it was converted to the glycol (VII) which was then oxidized.

(9) Abenius and Söderbaum, *Ber.*, **24**, 3034 (1891).

(10) Gray and Fuson, THIS JOURNAL, **56**, 1367 (1934). We are indebted to Dr. R. C. Fuson for a sample of the formoin.

(11) Fuson, Matuszeski and Gray, *ibid.*, **56**, 2100 (1934).

(12) Kohler and Baltzly, *ibid.*, **54**, 4024 (1932).

For this purpose 1.7 g. of the powdered quinoxaline was added to an excess of magnesium-free phenylmagnesium bromide and the reaction mixture on decomposition with sulfuric acid furnished 1.9 g. of the glycol. The material, which was sparingly soluble in the ordinary solvents, crystallized well from benzene and petroleum ether in fine needles melting at 163–164°.

Anal. Calcd. for $C_{28}H_{22}O_2N_2$: C, 80.4; H, 5.3. Found: C, 80.7; H, 5.4.

When the quinoxaline glycol (VII) suspended in warm glacial acetic acid was oxidized with the calculated amount of chromic oxide, the reaction mixture taken up in ether, washed with water and extracted with sodium carbonate, the extract furnished on acidification 3-phenylquinoxaline 2-carboxylic acid (VIII)—identified by comparison with a sample prepared according to the directions of Wahl.[13] From the ether, by evaporation and steam distillation, benzophenone was obtained.

In order to be certain that no benzoic acid (which would show the presence of a quinoxaline isomeric with VI but having the positions of the hydroxyl and carbonyl groups interchanged) had been formed in the oxidation and had been lost by admixture with the quinoxaline acid (VIII), we did a second oxidation of the glycol (VII) using a large excess of chromic acid. In this oxidation the products were benzophenone and the hydroxyquinoxaline (XV).[14] The hydroxyquinoxaline being soluble in alkali hydroxides and insoluble in alkali carbonates permitted a chemical separation from any benzoic acid which might have been formed. No benzoic acid was found. We had previously assured ourselves by a separate experiment that the quinoxaline acid (VIII) was converted to the hydroxyquinoxaline (XV) by chromic oxide.

Acylation.—The cyclic diacetate (XI, R = CH_3) was described by Abenius, who obtained it from the formoin and acetic anhydride.[5] We find that it is prepared in quantitative yield by treatment of the formoin with acetic anhydride and a little sulfuric acid. Other methods of preparation have been described in the introduction. The cyclic diacetate is stable and since it can be hydrolyzed to the formoin with alkali and converted to the furanone ethers (IX) with alcoholic acid, it is useful for storing the formoin. We were unable using alkali hydroxides to effect partial hydrolysis of the diacetate. This was possible, however, with *o*-phenylenediamine. Thus, when 1.7 g. of the diacetate in 25 cc. of boiling benzene was heated for two hours with 0.6 g. of the diamine and the solvent then removed *in vacuo*, a yellow solid was obtained. After crystallization from alcohol or acetic acid the pale yellow product melted at 198°.

Anal. Calcd. for $C_{18}H_{14}O_5$: C, 69.7; H, 4.5. Found: C, 69.7; H, 4.8.

The cyclic monoacetate (XII) is converted by acetic anhydride and sulfuric acid to the diacetate (XI, R = CH_3). With methyl alcohol and hydrochloric acid it furnishes the cyclic ether (IX, R = CH_3) and with alcoholic alkali it furnishes benzoylformoin.

When 2.7 g. of the formoin in 40 cc. of water containing 0.8 g. of sodium hydroxide was shaken for two hours with 2 cc. of acetic anhydride, the deep red color of the solution disappeared and 3.0 g. of a colorless solid precipitated. After crystallization from dilute alcohol the product melted at 109–110°.

Anal. Calcd. for $C_{18}H_{14}O_5$: C, 69.7; H, 4.5. Found: C, 69.7; H, 4.4.

The open chain monoacetate (XIV or its enol) is converted to the cyclic diacetate (XI, R = CH_3) by acetic anhydride and sulfuric acid and on treatment with *o*-phenylenediamine furnishes the hydroxyquinoxaline (XV).

When 7.3 g. of 2,4,6-trimethylbenzoyl chloride was added to a cold solution of 5.4 g. of the formoin in 40 cc. of pyridine and the reaction mixture was left for forty hours then decomposed with iced dilute hydrochloric acid a mixture of a solid and a sticky oil was obtained. Ether was added and the solid, 4.4 g., was separated by filtration. The ether extract, after washing with dilute acid, was evaporated and furnished an additional 3.1 g. of the solid. The product after crystallization from acetic acid melted at 145°.

Anal. Calcd. for $C_{36}H_{32}O_6$: C, 77.1; H, 5.7. Found: C, 76.9; H, 5.8.

The di-(2,4,6-trimethyl)-benzoate of benzoyl formoin (XVI, R = 2,4,6(CH_3)$_3C_6H_2$—) is sparingly soluble in the ordinary solvents. When 0.5 g. of the material was suspended in 20 cc. of boiling methyl alcohol containing 0.2 g. of *o*-phenylenediamine and boiled for four and one-half hours, the solution after the usual ether extraction gave 0.2 g. of the quinoxaline (XVII). The very sparingly soluble quinoxaline was crystallized from acetic acid and melted at 182–183°. (*Anal.* Calcd. for $C_{42}H_{36}O_4N_2$: C, 79.7; H, 5.7. Found: C, 79.2; H, 6.0.) The quinoxaline was oxidized with chromic oxide in hot glacial acetic acid and furnished the hydroxyquinoxaline (XV), m. p. and mixed m. p.

In one preparation of the diacyl derivative (XVI, R = 2,4,6-(CH_3)$_3C_6H_2$—) we obtained two products: the 145° compound already described and an isomer which melted at 189°. (*Anal.* Calcd. for $C_{36}H_{32}O_6$: C, 77.1; H, 5.7. Found: C, 76.8; H, 5.6.) The formation of the 189° isomer could not be repeated but we found that when 0.5 g. of the 145° isomer suspended in 25 cc. of methyl alcohol and 2 cc. of concd. hydrochloric acid was boiled for two hours, it was converted into the 189° isomer. The 189° isomer did not react with *o*-phenylenediamine after six hours of boiling in an alcoholic suspension.

The alkylation products of benzoylformoin can also be acetylated with acetic anhydride and sulfuric acid. The glycosidic monomethyl derivative (IX, R = CH_3) furnishes the acetate (XIII) already described by Abenius.[5] When 1.6 g. of the acetate (XIII) in benzene solution was boiled for an hour with 0.54 g. of *o*-phenylenediamine, it regenerated the methoxyl compound (IX, R = CH_3). The cyclic dialkyl derivatives (XVIII) undergo replacement of the glycosidic alkoxyl group by acetoxyl on treatment with acetic anhydride and sulfuric acid. Thus, when 3.0 g. of the dimethyl derivative (XVIII, R, R' = CH_3) was dissolved in 10 cc. of acetic anhydride containing a drop of sulfuric acid, the reaction mixture soon solidified. Decomposition with water furnished a quantitative yield of the methoxy acetate (XIX, R = CH_3) which melted, after crystallization from acetone, at 164–165° and which was

(13) Wahl, *Bull. soc. chim.*, [4] **1**, 461 (1907).

(14) Buraczewski and Marchlewski, *Ber.*, **34**, 4009 (1901).

unaffected by *o*-phenylenediamine in benzene solution. (*Anal.* Calcd. for $C_{19}H_{16}O_5$: C, 70.4; H, 4.9. Found: C, 70.3; H, 5.0.) In similar fashion, the diethyl derivative (XVIII, R, R' = C_2H_5) furnishes with acetic anhydride and sulfuric acid, the ethoxy acetate (XIX, R = C_2H_5) which, after crystallization from alcohol, melts at 133°. (*Anal.* Calcd. for $C_{20}H_{18}O_5$: C, 71.0; H, 5.3. Found: C, 70.7; H, 5.1.)

That it is the glycosidic alkyl group which is replaced on treatment of the dialkyl derivatives with acetic anhydride and sulfuric acid is shown by the fact that when the open chain monoalkyl derivatives of benzoylformoin (X) or (XXII) are treated with acetic anhydride and sulfuric acid they furnish the same cyclic alkoxy acetates (XIX) as are obtained from the dialkyl derivatives. Thus the methyl derivative (XXII, R = CH_3) furnishes (XIX, R = CH_3) while the ethyl derivative (XXII, R = C_2H_5) furnishes (XIX, R = C_2H_5).

Reactions with Hydrogen Bromide in Acetic Acid.—On treatment with this reagent the formoin and all of its derivatives which do not contain an alkyl group in the position occupied by R' in formula XVIII or R in formula XXII are destroyed and no definite products can be isolated. Derivatives of the formoin containing an alkyl group in the position indicated, for example the dialkyl derivatives (XVIII), the alkoxy acetates (XIX) and the monoalkyl derivatives (XXII) undergo replacement of alkoxyl, acetoxyl or hydroxyl by bromine with subsequent reduction of the resulting bromofuranones (XX) to the dimolecular products (XXI). Thus, the dimethyl derivative (XVIII, R,R' = CH_3), the methoxy acetate (XIX, R = CH_3) and the monomethyl derivative (XXII, R = CH_3), on solution in acetic acid and addition of a saturated solution of hydrobromic acid in acetic acid, gradually deposited a mixture of bromofuranone (XX, R = CH_3) and dimolecular product (XXI, R = CH_3). The dimolecular product interfered with the purification of the bromofuranone, so we contented ourselves with showing that the impure bromo compound could be converted to the dimolecular product by heating or by treatment in acetone solution with acidified potassium iodide. The dimolecular product was purified by crystallization from benzene and ligroin (70–90°) and from benzene alone. It melted at 226–227°.

Anal. Calcd. for $C_{34}H_{26}O_6$: C, 77.0; H, 4.9. Found: C, 76.9; H, 4.9.

The diethyl derivative (XVIII, R,R' = C_2H_5) and the monoethyl derivative (XXII, R = C_2H_5) with hydrogen bromide in glacial acetic acid furnish the ethoxy dimolecular product (XXI, R = C_2H_5). Purified by crystallization from benzene and ligroin, this dimolecular compound melted at 218–219°. (*Anal.* Calcd. for $C_{36}H_{30}O_6$: C, 77.4; H, 5.4. Found: C, 77.0; H, 5.5.) That it is the glycosidic alkyl group which is replaced in the reaction with hydrogen bromide is shown by the fact that ethyl methyl benzoylformoin (XVIII, R = C_2H_5, R' = CH_3) on treatment with this reagent furnishes the methoxy dimolecular product (XXI, R = CH_3).

The bromoethoxy compound (XXIV) has been described by Abenius.[5] It can be vacuum distilled without decomposition and is reduced by acidified potassium iodide to regenerate the monomethyl derivative (X or XXII, R = CH_3). With *o*-phenylenediamine the bromo compound gives the hydroxyquinoxaline (XV). Attempts to synthesize the bromo compound by adding ethyl bromide to diphenyl tetraketone were not successful.

The Action of Sodium Methylate on the Quinoxalines (VI) and (XXIII).—When 1.36 g. of the quinoxaline (VI) was dissolved in 30 cc. of methyl alcohol containing 1.6 g. of sodium an intensely purple colored solution resulted. The color of this solution faded very slowly in a stoppered container, rapidly when exposed to the air. In either case the odor of methyl benzoate was pronounced. After the color of the solution had bleached, water and ether were added. The aqueous layer was acidified, then made alkaline with sodium carbonate. The precipitate at this point consisted of 0.35 g. of the hydroxyquinoxaline (XV). The sodium carbonate filtrate was acidified and furnished 0.2 g. of benzoic acid. From the ethereal extract on evaporation there was obtained 0.5 g. of the quinoxalyl carbinol (XXV, R = H) which was purified by crystallization from ether and petroleum ether and from dilute methanol. It melted at 140–141° and could be distilled in a high vacuum.

Anal. Calcd. for $C_{15}H_{12}ON_2$: C, 76.3; H, 5.1. Found: C, 76.2; H, 5.2.

When the quinoxaline (XXIII)[2] was treated in similar fashion with sodium methylate, the alkaline solution was a vivid red. On working up the products of the reaction, methyl benzoate was identified by its odor, benzoic acid and the hydroxyquinoxaline (XV) by mixed melting points. The fourth product of the reaction, quinoxalyl carbinol methyl ether (XXV, R = CH_3), was obtained in much larger amounts than was the corresponding carbinol from the quinoxaline (VI). The ether was purified by high vacuum distillation and by crystallization from dilute methanol. It melted at 78–79°.

Anal. Calcd. for $C_{16}H_{14}ON_2$: C, 76.8; H, 5.6; OCH_3, 12.4. Found: C, 77.1; H, 5.7; OCH_3, 12.8.

The structures of the quinoxalyl carbinol and its methyl ether were established by etherification of the former to yield the latter and by oxidation of the carbinol to the known quinoxaline acid (VIII). Thus, 0.24 g. of the carbinol was dissolved in methyl iodide and boiled with a half gram of powdered sodium hydroxide for three hours. After removal of the methyl iodide, the reaction product was vacuum distilled and gave a quantitative yield of the methyl ether (XXV, R = CH_3). When 0.15 g. of the carbinol was oxidized in acetic acid with the calculated amount of chromic acid, the reaction mixture taken up in ether and washed with water, then extracted with sodium carbonate, the extract furnished on acidification 0.10 g. of the quinoxaline acid (VIII).

Summary

A description of the chemical behavior of benzoylformoin and its derivatives is presented. On the basis of this description it is concluded that the formoin and its open-chain monoalkyl derivatives are ene-diol hydroxyfuranone tautomers, while its cyclic mono- and dialkyl derivatives are alkoxyfuranones.

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