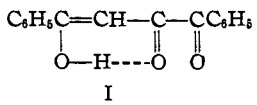
[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA]

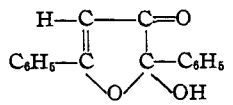
4-Benzoyl-2,5-diphenyl-2-hydroxyfuranone-3

BY ROBERT E. LUTZ, JAMES M. SMITH, JR.,[1] AND ALFRED H. STUART[2]

Substitution has a marked effect on the 1,2,4-triketone enol–hydroxyfuranone tautomerism. In the diphenyl series, the yellow chelated enol (I) is easily obtained and appears to be the dominant form in a mobile equilibrium (I $\rightleftarrows$ II), but the less stable colorless hydroxyfuranone (II) also can be isolated due to its lesser solubility.[3] The compounds with methyl[3c] or phenyl[3c,f] substituted at the chain position behave as if the cyclic



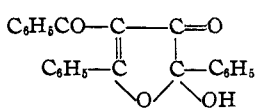
I



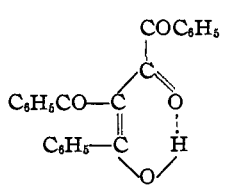
II

structures were fixed whereas the bromo derivative,[3d] while it appears also to exist in the cyclic form, functions in the sense of a mobile ring-chain tautomerism. The order of effectiveness of alkyl and halogen as substituents in promoting cyclization is similar to that in maleic and *cis*-aroylacrylic acids.[4]

This paper deals with benzoyl derivative (III–IV) which is of interest because the substituent is a strong negative group.

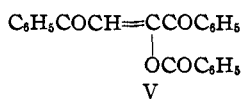


III

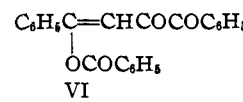


IV

The benzoyl derivative has already been mentioned in an earlier paper[3b]; it was obtained in the reaction between benzoyl chloride and the sodium salt of diphenyl butanetrione enol (I) and was recognized as a carbon–benzoyl compound. It was isolated in small yields in the form of the hydroxyfuranone benzoate (X) along with two enol-benzoates (V and VI); it was obtained free upon alkali hydrolysis.



V



VI

The compound evidently has the gross structure, III–IV, as is evident from the study of the reactions and derivatives described below and from the second synthesis which is described in the following paper.[5] It is colorless and does not react with ferric chloride. It is soluble in cold aqueous sodium bicarbonate solution and in this respect is unique since the other hydroxyfuranones so far studied are relatively weak acids. The high acidity must be accounted for in terms of the influence of the benzoyl group.

The methyl and ethyl ethers (VIII and XI) were made and proved to be interconvertible. The acetate and benzoate (IX and X) were obtained directly from the hydroxyfuranone (III) through reaction with acetic or benzoic anhydride and sulfuric acid. The benzoate (X) was transformed into either the methyl or ethyl ether upon acid catalytic alcoholysis. All four derivatives were hydrolyzed by acid or alkali to the hydroxyfuranone (III).

The cyclic structures of these derivatives are evident by analogy.[3] Furthermore, the methyl ether (VIII) reacted only very slowly with *o*-phenylenediamine to give the quinoxaline (XIII) in contrast with the supposed open-chain enol ether (XVII) and the hydroxyfuranone itself (III) which reacted readily under the same conditions. Also, the methyl ether upon ozonolysis gave methyl benzoate and benzoic and phenylglyoxylic acids, a result which excludes the open-chain 2-enol ether (XVIII) from consideration.

The silver salt reacted with benzoyl chloride to give the benzoate (X) and with methyl iodide to give the methyl ether (VIII). The yields were small but significant, and no evidence of carbon-acylation or alkylation was observed. The only other product isolated was the original hydroxyfuranone (III) which probably was formed by hydrolysis of the salt or some 4-enol acylate or ether. From these facts it would appear that the salts function as derivatives of a strongly acidic hydroxyfuranone (III) rather than as enolates

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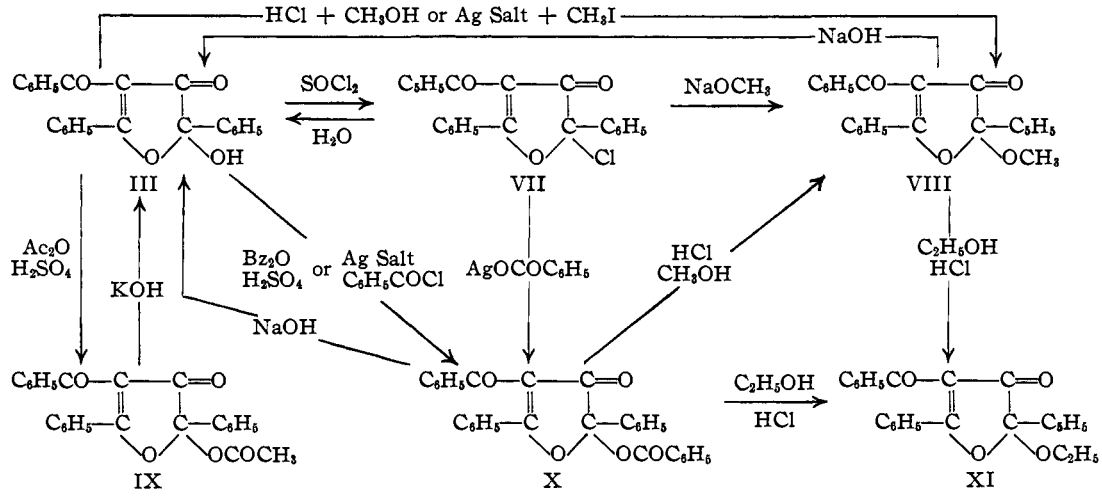
(2) Philip Francis du Pont Fellowship (1936–1937); present location, Schieffelin and Company, New York.

(3) (a) Lutz, Wilder and Parrish, THIS JOURNAL, **56**, 1980 (1934); Lutz and Stuart, *ibid.*, (b) **58**, 1885 (1936); **59**, (c) 2316; (d) 2322 (1937); (e) Kohler and Woodward, *ibid.*, **58**, 1933 (1936); (f) Kohler, Westheimer and Tishler, *ibid.*, **58**, 264 (1936).

(4) Lutz, *ibid.*, **52**, 3405 (1930); Lutz and Couper, *J. Org. Chem.*, **6**, 77 (1941); and references cited.

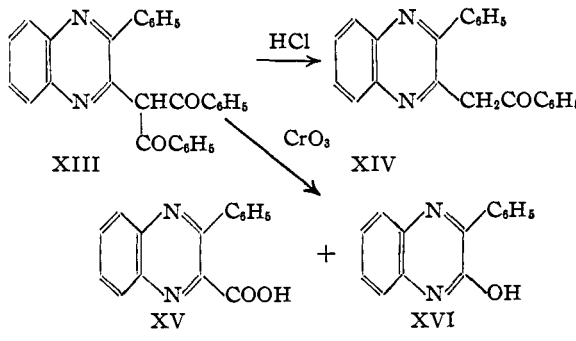
(5) Lutz and Smith, THIS JOURNAL, **63**, 1143 (1941).



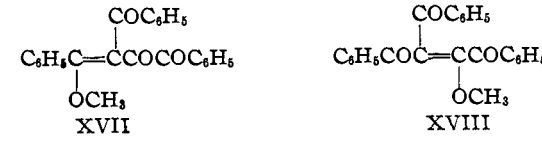
derived from IV. This corresponds to the behavior of the analogous 4-methyl and 4-phenyl hydroxydiphenylfuranones and is contrary to the behavior of the salts of the parent compound (I–II) and the monobromo derivative which function as enolates. However, in view of the low yields, perhaps only a limited significance should be attached to these results.

The chlorofuranone (VII) was produced by the action of phosphorus pentachloride or thionyl chloride on the hydroxyfuranone, but it could not be obtained in crystalline form. It behaved like an acid chloride, underwent hydrolysis with great ease, and reacted with sodium methylate and with silver benzoate, to give, respectively, the methoxy and benzoyloxyfuranones (VIII and X).

The hydroxyfuranone itself (III) in contrast with its derivatives reacted with *o*-phenylenediamine to give a quinoxaline (XIII) the structure of which was demonstrated by β-diketone cleavage to 2-phenacyl-3-phenylquinoxaline (XIV) and by chromic acid oxidation to 2-carboxy-3-phenyl and 2-hydroxy-3-phenylquinoxalines (XV and XVI). The quinoxalyl-β-diketone (XIII) gave a characteristic slow and deepening color reaction with ferric chloride. The enol form (yellow) was obtained upon acidification of a sodium methylate solution; it gave an immediate deep color reaction with ferric chloride; however, it was unstable and reverted to the keto form upon standing. All attempts to obtain derivatives failed, the result usually being hydrolytic cleavage which occurs with a facility characteristic of this type of β-diketone (*cf.* dibenzoylphenylmethane[6]).



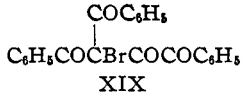
The hydroxyfuranone (III) reacted rapidly with diazomethane but did not give the methoxyfuranone which crystallizes readily under the conditions involved and undoubtedly would have been detected if present in significant amounts. The non-crystalline product appeared to consist chiefly of the enol ether XVII because of: (a) the ease of hydrolysis to the hydroxyfuranone, III; (b) methanolysis by methanolic hydrogen chloride to the cyclic ether, VIII; (c) the rapid reaction with *o*-phenylenediamine to give the quinoxalyl-β-diketone, XIII; (d) ozonolysis to methyl benzoate and phenylglyoxylic acid (the failure to detect phenylglyoxylic methyl ester among the products indicated the absence of significant amounts of the isomeric enol ether, XVIII); and (e) the parallelism of the results with those obtained in the 1,4-diphenylbutanetrione enol series (I–II).[3b] Unfortunately, the difficulty of obtaining material in quantity prevented the completion of this phase of the investigation, and a



(6) Prinz, *J. prakt. Chem.*, **24**, 353 (1881).

general study of the diazomethane reaction in this and related fields is being initiated.

The K. Meyer titration of the hydroxyfuranone (III) with bromine in the usual way in ethanol at $-19°$ gave results analogous to those obtained with other hydroxyfuranones. About 60% of one equivalent of bromine was absorbed over a period of one second and the reaction was complete within two minutes. The rate of bromination, while high, was definitely lower than that for an enol and was comparable with that for 4-substituted hydroxyfuranones.[3c,d] The resulting bromotetraketone (XIX) was very easily reduced



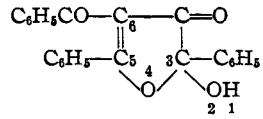
XIX

back to the hydroxyfuranone by means of potassium iodide. Also, reductive elimination of the bromine occurred with methanolic hydrogen chloride, giving the methyl ether (VIII), and with *o*-phenylenediamine, giving the quinoxalyl-β-diketone (XIII).

One striking property of the hydroxyfuranone (III) deserves emphasis, namely, the stability toward alkali. The characteristic β-diketone cleavage could be accomplished only by drastic treatment with 33% methanolic potassium hydroxide, the products identified being benzoic acid, phenylglyoxylic acid and glyoxal. The hydroxyfuranone is stable also toward acid hydrolytic agents. It would seem *a priori* that if the compound had the open-chain structure (IV) or involved this form in a mobile tautomeric equilibrium, it would be cleaved easily under these conditions as are the quinoxalyl-β-diketone (XIII) and various di- and triaroylmethanes,[6,7] which are incapable of cyclization to stable hydroxyfuranones. In fact, certain reactions which should lead to the hypothetical open-chain enol (IV) or a derivative involve fission instead, *i. e.*, the action of sodium hydroxide, sodium methoxide, and ammonia on bromotribenzoylethylene.[5] The relative stability toward alkali of the compound under discussion therefore supports the fixed hydroxyfuranone structure.

The positive evidence for the cyclic structure (III) may be summarized as: (a) lack of color, (b) failure to react with ferric chloride, (c) resistance toward alkaline hydrolytic cleavage, (d) the low rate of bromination, and (e) the reactions of the silver salt. In respect to these reactions, the 4-benzoyl compound is like the 4-methyl and 4-phenyl analogs and unlike diphenylbutanetrione enol (I).

Reactions which might be interpreted as involving the open-chain form are: (a) the formation of the open-chain bromotetraketone, (b) the reaction with *o*-phenylenediamine, and (c) the reaction with diazomethane. However, these three reactions may also be interpreted as direct reactions of the fixed cyclic structure (III), as follows: Bromination may involve reaction at points, 1,6, 2,6, 4,6, or 5,6 in the numbered formula below.



The *o*-phenylenediamine reaction may involve the furanone carbonyl group and the hydroxyl or lactone bridge oxygen. And diazomethane may undergo a net 1,4-reaction with the system $\overset{6}{C}=\overset{5}{C}-\overset{4}{O}-\overset{3}{C}-\overset{2\,1}{OH}$, by a mechanism analogous to that involved in 1,2-reaction with a simple enolic or phenolic group, $\overset{4}{C}=\overset{3}{C}-\overset{2\,1}{OH}$.

Expression of the above two groups of reactions in terms of a mobile equilibrium between the hydroxyfuranone (III) and the open-chain enol (IV) seems to be questionable in view of the positive evidence for the fixed cyclic structure and the lack of unequivocal evidence to the contrary. From the point of view of resonance in the anion, involving the open-chain enol as one of the possible structural phases, a bonding of some sort still must exist between positions 3 and 4 in the numbered formula above, with the 4-oxygen fixed in a modified but, nevertheless, cyclic arrangement. We have, therefore, adopted the simple cyclic formula (III) and the expression of some of the reactions in terms of conjugation effects, subject to the equivalent expression in terms of electronic and resonance concepts.

Experimental[8]

4-Benzoyl-2,5-diphenyl-2-hydroxyfuranone-3 (III).—A typical preparative procedure is as follows. Thirty cc. of benzoyl chloride was added dropwise to a mechanically stirred suspension of 20 g. of diphenylbutanetrione sodium enolate in 100 cc. of dry isopropyl ether. After refluxing for three hours and filtering from sodium chloride, some of the benzoate, V, crystallized and was separated by filtration. The solution was evaporated and the residual oil added slowly to 200 cc. of 10% sodium hydroxide in

(7) Meyer, *Monatsh.*, **28**, 1211, 1231 (1907).

(8) All melting points are corrected. We are indebted to Mrs. James A. L. Mathers for several of the microanalyses.

80% methanol, with cooling.[9] After standing for three hours, the solution was heated to 60° to complete the hydrolysis of the benzoates. The mixture partially crystallized (sodium benzoate) and was diluted with 2 liters of water; the resulting turbid solution was then acidified. The product liberated was extracted by means of ether. The ether solution was shaken with 25 portions of saturated sodium bicarbonate, which was required to remove all of the benzoylhydroxyfuranone. The product along with some benzoic acid was liberated by treatment with hydrochloric acid; this was filtered and washed with hot water to remove the benzoic acid. The yield of III was 5 g. (15%). It was crystallized repeatedly from ethyl acetate–petroleum ether mixtures and melted at 166°.

Anal. Calcd. for $C_{23}H_{16}O_4$: C, 77.5; H, 4.5. Found: C, 77.4; H, 4.4.

The sodium salt was prepared as follows: 1 g. of the hydroxyfuranone was added to a solution of one equivalent (0.08 g.) of sodium in 5 cc. of methanol (chilled to 0°). Upon concentrating 1.3 g. of white crystalline precipitate appeared. This was washed with a small amount of cold methanol, dried, and used without further purification.

The silver salt was obtained as an unstable gray precipitate when the calculated amount of 2% silver nitrate solution was added to a cold aqueous solution of the sodium salt. It was made up fresh for use and was washed with water and then with ether. It darkened rapidly when exposed to light.

The K. Meyer titration of the hydroxyfuranone (III) at −16 to −19° in ethanol was carried out in the usual way. The percentage reaction after several time interludes was determined by addition of β-naphthol to eliminate excess bromine, liberation of iodine by potassium iodide, and titration in the usual way with sodium thiosulfate. After one second between 56 and 60% of one molecule of bromine was used up; after five seconds, 74%; and in two minutes, 99%. In the latter run, the product was isolated by diluting the solution with water after titration, boiling off the alcohol, and extracting with ether; the hydroxyfuranone (III) was recovered.

Hydrolysis.—The hydroxyfuranone (III) was recovered unchanged after being subjected to the action of refluxing 80% ethanol acidified with hydrochloric acid (three hours). Likewise, refluxing 80% ethanolic sodium carbonate (two hours) was without effect.

Hydrolysis was accomplished as follows. A solution of 1 g. of III in 50 cc. of 33% potassium hydroxide in 50% methanol was refluxed for three hours. The solution was diluted to 100 cc. with ice water and then extracted with five portions of ether. From the alkaline solution upon acidification, 0.09 g. of the hydroxyfuranone (III) was recovered. From the filtrate a small amount of benzoic acid (0.12 g.) was isolated by extraction with ether; then upon addition of semicarbazide hydrochloride, 0.1 g. of phenylglyoxylic acid semicarbazone precipitated. From the non-acidic oils held in the first ether extraction, no crystalline product was obtained; however, treatment in methanol with semicarbazide hydrochloride produced two semicarbazones which were separated by digestion with ethanol. The insoluble material was purified by washing with hot ethanol and ether, and melted with decomposition at 259°. The properties of the compound agree closely with those of **glyoxal disemicarbazone**[10] and the identity was established by analysis (calcd. $C_4H_8O_2N_6$: C, 27.9; H, 4.7; N, 48.8. Found: C, 22.3; H, 4.95; N, 44.4). This sample, from its melting point and analysis, evidently contained a small amount of an impurity. The **soluble semicarbazone** (the major product, 0.75 g.) was not identified. It was repeatedly crystallized from ethanol and melted at 285° (Found: C, 78.1; H, 4.7; N, 7.7, 7.8).

4-Benzoyl-2-benzoyloxy-2,5-diphenylfuranone-3 (X) was first obtained by fractional crystallization of the products obtained directly from the benzoylation of diphenylbutanetrione sodium enolate in isopropyl ether. It was obtained also by the action of benzoic anhydride and sulfuric acid on the hydroxyfuranone (III) as follows. A mixture of 0.5 g. of III and 2 g. of benzoic anhydride was fused and 2 drops of concd. sulfuric acid was added. After standing for one hour, the mixture was hydrolyzed by sodium bicarbonate solution. A white crystalline precipitate was obtained of nearly pure X in a yield of 0.45 g. It was crystallized repeatedly from ethanol and melted at 182°.

Anal. Calcd. for $C_{30}H_{20}O_5$: C, 78.2; H, 4.4. Found: C, 78.1, 78.1, 78.2, 78.1, 78.4; H, 4.7, 4.4, 4.5, 4.7, 4.6.

The large number of analyses were run because this compound when first obtained was thought to be the hydroxyfuranone (III) whose calcd. analysis was C, 77.5; H, 4.5. It was this series of analyses which led to the elucidation of the structure.

The benzoate (X) was obtained also in 20% yield by the action of 0.5 cc. of benzoyl chloride on 0.7 g. of the silver salt of III in 50 cc. of absolute isopropyl ether (refluxed for two hours). Unchanged III was recovered in the experiment (40%). It was shown that benzoyl chloride under comparable conditions was without effect on III itself.

2-Acetoxy-4-benzoyl-2,5-diphenylfuranone-3 (IX).—A suspension of III in 20 cc. of acetic anhydride containing one drop of concd. sulfuric acid was allowed to stand for thirty minutes at 25°. The mixture was then hydrolyzed in ice water and the oil obtained was separated and dissolved in isopropanol from which the methoxy compound crystallized. Upon repeated crystallization from ethyl acetate–ligroin mixtures, it melted at 120.5°.

Anal. Calcd. for $C_{25}H_{18}O_5$: C, 75.3; H, 4.55. Found: C, 75.1; H, 4.56.

Hydrolysis to the hydroxyfuranone (III) was effected by treatment with 10% potassium hydroxide in 80% methanol at 60° for one hour.

4-Benzoyl-2,5-diphenyl-2-methoxyfuranone-3 (VIII).—A suspension of the hydroxyfuranone (III) or its benzoate (X) in saturated methanolic hydrogen chloride was allowed to stand for forty-eight hours. Evaporation of the solution left a solid residue which was crystallized from methanol. It melted at 131°.

Anal. Calcd. for $C_{24}H_{18}O_4$: C, 77.8; H, 4.9. Found: C, 78.0; H, 5.1.

(9) *Cf.* the formation of a by-product under different manipulation [Lutz and Smith, THIS JOURNAL, **61**, 1465 (1939)].

(10) Harris and Temme, *Ber.*, **40**, 171 (1907); Kötz, *J. prakt. Chem.*, **90**, 312 (1914).

The methyl derivative (VIII) was obtained also as follows. A suspension of 2.8 g. of the silver salt of III in 75 cc. of absolute isopropyl ether and 0.75 cc. of methyl iodide was refluxed for five hours and the resulting silver iodide removed by filtration. Acidic material was removed by extraction with 5% sodium carbonate and gave 0.5 g. of III (yield, 25%). From the non-acidic material, 0.3 g. of nearly pure VIII was isolated (yield, 15%).

A solution of 0.2 g. of the methoxy compound and 0.1 g. of *o*-phenylenediamine in 12 cc. of ethanol was refluxed for two hours and 0.12 g. of unchanged material was recovered. From the filtrate 0.05 g. of the quinoxaline (XIII) was isolated and identified.

Ozonization of 1.25 g. of VIII in 30 cc. of dry chloroform gave a non-acidic oil which on hydrolysis with alcoholic potassium hydroxide gave 0.15 g. of benzoic acid (37%) and no phenylglyoxylic acid semicarbazone. The acidic fraction of the products yielded 0.05 g. of benzoic acid and 0.1 g. of phenylglyoxylic acid semicarbazone.

4-Benzoyl-2,5-diphenyl-2-ethoxyfuranone-3 (XI) was prepared as above, using absolute ethanol as solvent and starting with the hydroxyfuranone benzoate (X). It was obtained as an oil upon evaporation of the solution, and crystallized from a petroleum ether–ethyl acetate mixture. It melted at 83°.

Anal. Calcd. for $C_{25}H_{20}O_4$: C, 78.1; H, 5.3. Found: C, 78.0; H, 5.5.

4-Benzoyl-2-chloro-2,5-diphenylfuranone-3 (VII).—This compound was not isolated in crystalline form and characterized but its existence was demonstrated by the following experiments. Treatment of 0.5 g. of the hydroxyfuranone with 15 cc. of thionyl chloride (refluxing for one hour) and evaporation of the thionyl chloride by a stream of dry air (warm water-bath) gave an oil which was cooled to 0°. After addition of excess cold sodium methylate solution and standing at 0° for one hour, 0.2 g. of the methoxy compound (VIII) had crystallized, and from the solution an additional 0.23 g. was isolated (yield, 83%). In a control experiment, it was shown that no methoxyfuranone was formed when thionyl chloride was added to a methanol solution of the hydroxyfuranone (III) under comparable conditions.

3 - Benzoyl - 3 - bromo - 1,4 - diphenylbutanetrione-1,2,4 (XIX).—A solution of 0.45 g. of bromine in ethanol, cooled to 0°, was added to a solution of 1 g. of III in 25 cc. of ethanol, also at 0°. Yellow crystals soon deposited; yield, 0.98 g. (81%). Upon crystallization from ethanol, it melted at 114.5°.

Anal. Calcd. for $C_{25}H_{15}O_4Br$: C, 63.4; H, 3.5. Found: C, 63.5; H, 3.3.

Reduction was effected as described above by means of potassium iodide. The action of methanolic hydrogen chloride (twelve hours) gave 4-benzoyl-2-methoxy-2,5-diphenylfuranone-3 (VIII) which was identified by mixture melting point. From the filtrate an unidentified by-product melting at 110° was obtained in small amounts.

2-[Dibenzoylmethyl]-3-phenylquinoxaline (XIII).—A solution of 0.1 g. of III and 0.1 g. of *o*-phenylenediamine in 10 cc. of ethanol was refluxed for one hour. Upon concentrating the solution and cooling, 0.1 g. of long colorless needles appeared (yield, 83%). Upon recrystallization from ethanol, it melted at 157°.

Anal. Calcd. for $C_{29}H_{20}O_2N_2$: N, 6.54. Found: N, 6.70.

The same compound was obtained when either the bromotetraketone (XIX) or the enol ether (XVII) was used in the above experiment (in the latter case, the reaction proceeded immediately at room temperature). When treated with sodium methylate (fifteen minutes), a yellow solid melting at 60–65° was recovered. It gave an immediate red coloration with ferric chloride. Upon crystallization, the melting point rose to that of the keto form (XIII) which did not then give an immediate test with ferric chloride but did so upon standing for 12 hours.

Hydrolysis with the formation of 2-phenyl-3-phenacylquinoxaline (XIV) occurred when XIII was treated with a boiling solution of hydroxylamine hydrochloride and an excess of sodium acetate, or with a solution of phenylhydrazine under similar conditions. Also when a solution of 0.1 g. of XIII in 10 cc. of 75% ethanol and 10 drops of concd. hydrochloric acid was refluxed for one hour, 0.07 g. (93%) of orange colored needles was obtained; melting point 166°; identified as XIV by mixture melting point with an authentic sample.[3b] From the filtrate, a small amount of benzoic acid was isolated and identified.

Oxidation of 0.9 g. of XIII in 10 cc. of concd. acetic acid with 0.42 g. of chromic acid in 3 cc. of 50% acetic acid (boiling for two minutes) gave 0.15 g. of 2-hydroxy-3-phenylquinoxaline (XVI) and 0.05 g. of 2-carboxy-3-phenylquinoxaline (XV) and 0.3 g. of benzoic acid. These products were separated by difference in solubility in sodium bicarbonate and in hot water.

3 - Benzoyl - 1,4 - diphenyl - 4 - methoxybutenedione-1,2 (XVII).—This enol ether was obtained as an oil and was not purified or characterized. Its existence was assumed from the following experiments.

An ether solution of diazomethane was allowed to react with a sample of III, and evaporation of the solution gave an oil.

A solution of 0.13 g. of this oil and 0.15 g. of *o*-phenylenediamine in ethanol at 25° gave immediately 0.1 g. of the quinoxaline (XIII); yield, 66%. Attempts to isolate a 2-enol ether (XVIII) from the filtrate were unsuccessful, and ozonization of the residual oils gave inconclusive results.

Ozonization of the product of reaction between diazomethane and 2 g. of III was carried out in 40 cc. of dry chloroform at 0° for five hours. Evaporation of the solvent and decomposition with water was followed by treatment with sodium bicarbonate solution and then extraction with ether. From the sodium bicarbonate solution upon addition of hydrochloric acid 0.4 g. of benzoic acid crystallized (30% of the calculated two equivalents); from the filtrate upon addition of semicarbazide hydrochloride 0.55 g. of phenylglyoxylic acid semicarbazone was obtained (24% of two equivalents). From the ether extracts upon evaporation, an oil was obtained which evidently consisted of a mobile ester; upon hydrolysis with 10% potassium hydroxide in 90% methanol (refluxing for thirty minutes), 0.5 g. of benzoic acid was isolated; and no phenylglyoxylic acid could be detected. The ester fraction therefore consisted chiefly of methyl benzoate.

Hydrolysis of samples of the oil (XVII) by means of concd. acetic and hydrochloric acids (refluxing) and by

means of 2% potassium hydroxide in 70% methanol (refluxing) gave 50% yields of the hydroxyfuranone (III). The action of sodium methylate (at 25°), however, produced an unidentified compound melting at 119–121°.

The action of methanolic hydrogen chloride (twelve hours at room temperature) gave only 4-benzoyl-2,5-diphenyl-2-methoxyfuranone-3 (VIII).

Summary

4-Benzoyl-2,5-diphenyl-2-hydroxyfuranone-3 has been synthesized by carbon benzoylation of 1,4-diphenylbutane-1,2,4-trione sodium enolate. It is strongly acidic and remarkably stable toward alkali. The formation, interconversion and hydrolysis of the methyl and ethyl ethers and the acetyl and benzoyl derivatives, as well as the preparation and reactions of the chloride, have been described. The reactions of the silver salt take place in the sense of the hydroxyfuranone rather than the open-chain triketone enolate form.

Reaction with *o*-phenylenediamine gave an easily hydrolyzable quinoxalyl-β-diketone. The action of diazomethane produces an open-chain enol ether. Bromination gives the open-chain bromotetraketone.

The question of structure and the triketone enol–hydroxyfuranone tautomerism was discussed. The evidence was regarded as favoring the hydroxyfuranone formulation.

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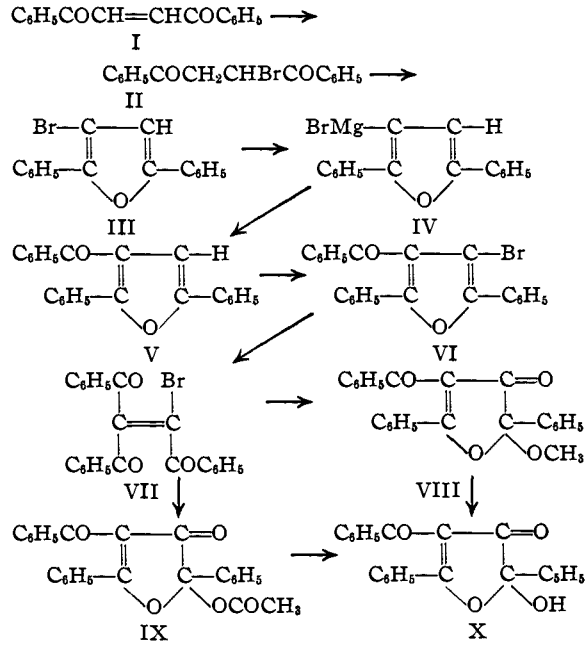
[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA]

The Synthesis of 4-Benzoyl-2,5-diphenyl-2-hydroxyfuranone-3 through Benzoyldiphenylfuran and Bromotribenzoylethylene

BY ROBERT E. LUTZ AND JAMES M. SMITH, JR.[1]

This synthesis by a second path[2] was carried out in order to demonstrate independently the nature of the benzoyl group attachment. The compounds and reactions involved are of interest in connection with the investigation now in progress on the unsaturated triketones and related substances.

The new synthesis started with dibenzoylethylene (I) which was converted through the bromodiketone (II) into the bromofuran (III). Diphenylfurylmagnesium bromide (IV) was then made according to the method described by Woodward,[3] and this, when treated with benzoic anhydride, gave β-benzoyldiphenylfuran (V, known[4]). Bromination in carbon tetrachloride gave the bromofuran (VI, also known[4]), and oxidation by nitric acid produced the corresponding unsaturated 1,4-diketone (VII, new). The latter compound was converted by methanolic hydrogen chloride into the methyl ether of the hydroxyfuranone (VIII) and by acetic anhydride and sulfuric acid into the acetate (IX). Analogy is to be found for these two reactions in the similar transformations of dibenzoylchloroethylene into



2,5-diphenyl-2-ethoxyfuranone-3[5] and of bromodibenzoylmethylethylene into 2,5-diphenyl-4-methyl-2-acetoxyfuranone-3.[6] These reactions evidently involve 1,4-addition of the reagent followed by hydrolysis and elimination of the hydrogen bromide, and cyclization. The two

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(2) *Cf.* the preceding paper; Lutz, Smith and Stuart, THIS JOURNAL, **63**, 1143 (1941).

(3) Woodward, Dissertation, Harvard University, 1937.

(4) Kohler and Jones, THIS JOURNAL, **41**, 1249 (1919).

(5) Lutz, Wilder and Parrish, *ibid.*, **56**, 1980 (1934).

(6) Lutz and McGinn, unpublished results obtained subsequent to this research.