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

2-Hydroxy-4-methyl-2,5-diphenylfuranone-3

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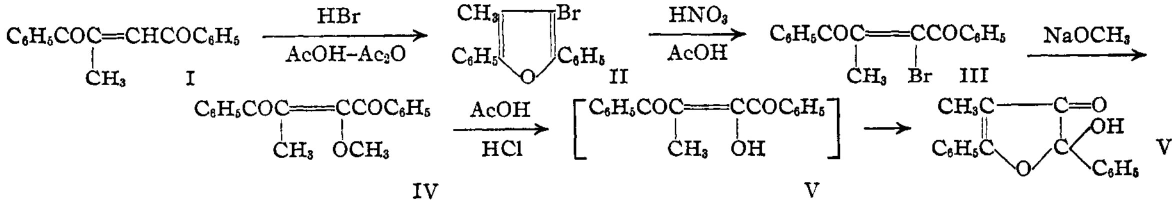
We have extended the investigations on 1,4-diphenyl-1,2,4-butanetrione to include the 3-methyl derivative in order to study the effect of substitution of a small alkyl group on the reactions of the system and on the ring-chain tautomerism involved. The 3-methyl derivative, as preliminary experiments have shown,[1] is like the triphenyl compound (XXII),[2] and appears to exist only in the cyclic or hydroxyfuranone form VI in contrast with diphenylbutanetrione itself which apparently can exist and react in both the cyclic and the open-chain enol forms.

The methyl compound is best prepared by alkylation of diphenylbutanetrione silver enolate with methyl iodide.[1a] A new synthesis was achieved as follows: dibenzoylmethylethylene, I, prepared from mesaconic acid through the Friedel and Crafts reaction, was converted into 3-bromo-4-methyl-2,5-diphenylfuran, II, by the action of hydrobromic acid in glacial acetic acid and acetic anhydride. The furan was then oxidized by means of the nitric–glacial acetic acid reagent to dibenzoylbromomethylethylene, III. Subsequent treatment of this with sodium methylate gave the enol methyl ether, dibenzoylmethoxymethylethylene, IV, the structure of which was shown by ozonolysis to benzoic acid and phenylglyoxylic methyl ester. Hydrolysis of the enol ether with acetic and hydrochloric acid gave the hydroxyfuranone, presumably through the enol, V, as an intermediate. This new synthesis, while it shows the location of the methyl group, is inferior as a method of preparation.



The hydroxyfuranone is colorless and does not react readily with *o*-phenylenediamine. It is soluble in alkali, forms a sodium and a silver derivative, and absorbs one molecule of bromine with great rapidity, yet it reacts neither with ferric chloride nor with diazomethane as does diphenylbutanetrione enol. The cyclic rather than the open-chain formulation best accounts for these properties. The absence of any significant amount of enol in mobile equilibrium is implied in the inability to react with diazomethane (it is conceivable that low concentration of the enol and steric factors account for this; however, with bromine in place of methyl no hindrance to the reaction with diazomethane is encountered).[3]

Ozonolysis of the compound yields almost two equivalents of benzoic acid and almost no phenylglyoxylic acid, in contrast with diphenylbutanetrione enol which gives these two acids in approximately equivalent amounts. This also supports the cyclic hydroxyfuranone structure.

As would be expected, the hydroxyfuranone is etherified easily with alcoholic hydrogen chloride. The cyclic structures of the ethers, VII and VIII, are evident enough by analogy[1,2] and are supported by ozonization of the methyl ether VII to benzoic acid and methyl benzoate, and by the failure of this ether to react with *o*-phenylenediamine. These relationships, including interconversions and hydrolysis, are outlined in the diagram.

Acetic or benzoic anhydride (with sulfuric acid) converts the hydroxyfuranone into, respectively, the acetate or benzoate, IX and X, while thionyl chloride or acetyl or benzoyl chloride (with sulfuric acid) produces the chlorofuranone, XI, as outlined in the last part of the diagram. The chlorofuranone is easily converted by boiling ethanol into the ethoxyfuranone and by means of silver benzoate into the corresponding benzoyloxyfuranone. In view of these simple and direct relationships, and the close analogy between these

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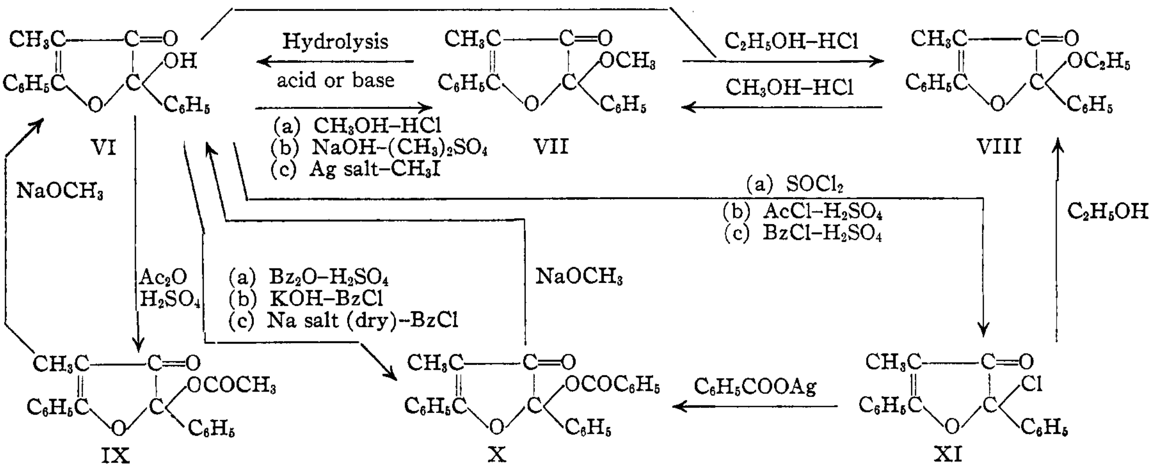
[1] (a) Lutz and Stuart, THIS JOURNAL, **58**, 1885 (1936). *Cf.* also (b) Kohler and Woodward, *ibid.*, **58**, 1933 (1936).

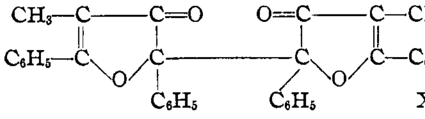
[2] Kohler, Westheimer and Tishler, *ibid.*, **58**, 264 (1936).

[3] *Cf.* Lutz and Stuart, *ibid.*, **59**, 2322 (1937).

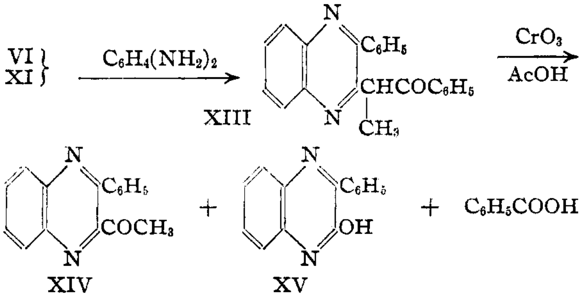


compounds and the di- and triphenylhydroxyfuranones and their derivatives, there can be no doubt as to these formulations.

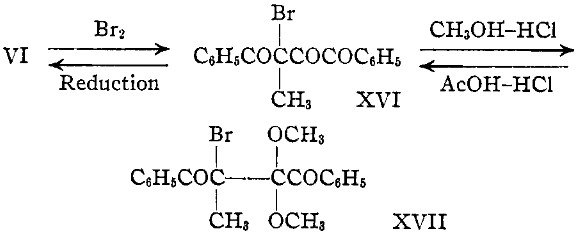
The hydroxyfuranone is not reduced by sodium hydrosulfite, nor by stannous chloride, but when heated with zinc and acetic acid, it is converted into an oil from which a small amount of the dimolecular product XII was obtained. This product was obtained also from the chlorofuranone XI, in poor yield by the action of zinc and acetic acid or catalytic hydrogen, and in good yield by the use of copper bronze.


XII

The hydroxyfuranone, while it reacts with *o*-phenylenediamine to give the quinoxaline, XIII, does so slowly in contrast with diphenylbutanetrione enol which reacts very readily. This difference in reactivity is consistent with the cyclic and open-chain structures presumably involved in the two cases. The chlorofuranone, XI, reacts rapidly, as would be expected in view of its active halogen, with loss of chlorine, to give the same quinoxaline, XIII. The structure of the quinoxaline was shown by oxidative degradation with chromic acid to benzoic acid and a mixture of acetyl- and hydroxyphenylquinoxalines XIV and XV (known).[4]



The hydroxyfuranone, VI, reacts readily with one equivalent of bromine to give the bromo triketone, XVI, an almost colorless solid which in solution shows the bright yellow color characteristic of α-diketones. The bromo triketone is converted by methanolic hydrogen chloride into an acetal which in turn is readily hydrolyzed back to the bromo triketone by acids.


$$\mathrm{VI}\ \underset{\text{Reduction}}{\overset{Br_2}{\rightleftarrows}}\ C_6H_5CO\overset{Br}{\underset{CH_3}{C}}COCOC_6H_5\ \underset{AcOH-HCl}{\overset{CH_3OH-HCl}{\rightleftarrows}}\qquad \mathrm{XVI}$$

$$C_6H_5CO\overset{Br}{\underset{CH_3}{C}}-\overset{OCH_3}{\underset{OCH_3}{C}}COC_6H_5\qquad \mathrm{XVII}$$

The bromo triketone is reduced easily by means of sodium hydrosulfite, potassium iodide, or sulfur dioxide, to the hydroxyfuranone, VI. Treatment with *o*-phenylenediamine also brings about reduction through loss of halogen by bromination of excess reagent, the quinoxaline XIII being produced. The bromo triketone has a similar brominating action on β-naphthol in chloroform solution containing hydrogen bromide, but it is stable in the absence of hydrogen bromide which appears to function as a catalyst. From these facts it is evident that the halogen has a degree of reactivity approaching but not equal that of hypohalite halogen.[5]

The speed of bromination of the hydroxyfur-

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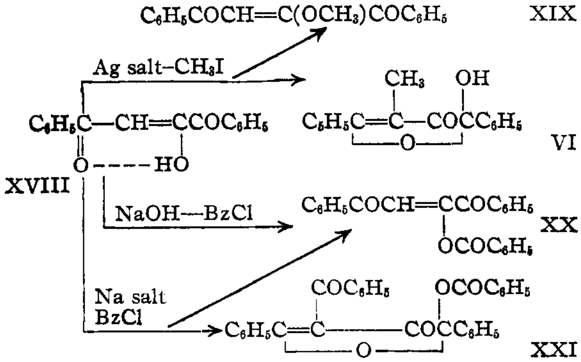
[4] (a) Blatt, THIS JOURNAL, **57**, 1103 (1935); (b) Sachs and Rohmer, *Ber.* **35**, 3318 (1902).

[5] *Cf.* Howk and McElvain, THIS JOURNAL, **54**, 285 (1932); **55**, 3372 (1933).

anone, while great, appears to be less than that for true enols. The reaction in ethanol at $-15°$ proceeds to 85% of completion within two seconds, and is complete within one minute. Hydroxytriphenylfuranone, XXII, however, where phenyl replaces the methyl, reacts to only 9% of completion under comparable conditions. Granting the cyclic formulations of these compounds, the mechanism of bromination becomes of interest since the rate of reaction, in the case of the methyldiphenyl compound, VI, at least, appears too great to be accounted for in terms of shift to the open-chain enol form during reaction. There is present in the hydroxyfuranone the conjugated system[6] C=C—O—C—OH which is in a sense analogous to the system C=C—C=C—OH in phenol. Whatever the mechanism of bromination of phenols or enols, a similar scheme might apply also to the hydroxyfuranone system.

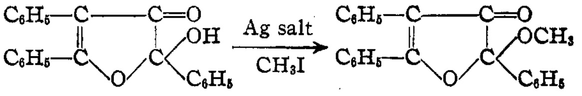
The hydroxyfuranone is quite soluble in aqueous sodium hydroxide solution and is recovered upon subsequent hydrolysis under carefully controlled conditions. The action of dimethyl sulfate on a strongly alkaline solution of the compound leads to the methoxyfuranone, whereas in contrast diphenylbutanetrione sodium enolate does not react under these conditions. Benzoyl chloride reacts with the strongly alkaline solutions, precipitating the hydroxyfuranone, whereas diphenylbutanetrione enolate solutions under these conditions give the enol benzoate XX. These reactions indicate that the hydroxyfuranone structure is maintained, even in strongly alkaline solution, and points to a relatively high degree of acidity in the hydroxyl group of the hydroxyfuranone comparable with that of true enols.



The sodium derivative does not crystallize out from alcohol solution, as does the diphenylbutanetrione sodium enolate, but it may be obtained as a pale yellowish solid by the action of metallic sodium on an ether solution of the hydroxyfuranone. In the dry state the salt is unreactive toward methyl iodide but reacts with benzoyl chloride in dry inert solvent to give the benzoyloxyfuranone. This result is to be contrasted with that on the brilliant yellow sodium derivative of diphenylbutanetrione enol which in dry solvents reacts like a true enolate to give the enol benzoate XX and a carbon benzoyl product XXI.[7]

The silver salt of the hydroxyfuranone was obtained as an unstable gray precipitate when an aqueous solution of the sodium salt, however prepared, was treated with silver nitrate. It reacted readily with methyl iodide to give as the sole product the methoxyfuranone, in contrast with the brilliant yellow diphenylbutanetrione silver enolate which gives largely the carbon-alkylation product, VI, together with small amounts of the enol ether, dibenzoylmethoxyethylene, XIX.

Incidentally, we find that hydroxytriphenylfuranone, XXII, studied by Kohler, Westheimer and Tishler, is also readily soluble directly in alkali and gives an unstable grayish silver salt which reacts with methyl iodide to give methoxytriphenylfuranone XXIII.



XXII XXIII

There proves to be a practically complete parallelism between the reactions of our hydroxyfuranone, VI, and those of the triphenyl compound, XXII, even though there is a considerable difference between the two substituent groups, methyl and phenyl.

It would appear from the many consistent and simple relationships, described above, that the hydroxyfuranone structure is involved exclusively in this series of compounds including the metal derivatives, in contrast with diphenylbutanetrione enol which apparently exists and reacts both in cyclic and open-chain forms and gives true metal enolates. The reactions of the sodium derivative of hydroxytriphenylfuranone, however, have been interpreted by Kohler and co-workers in terms of equilibrium in the anion between the cyclic and the two possible open-chain enolate forms, an

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(6) Using the term in the broad sense [*cf.* Lutz, Wilder and Parrish, THIS JOURNAL, **56**, 1983 (1934) footnote 8.]

(7) We are certain of the nature and structure of this compound but publication of details will be postponed until the work in this series has been completed (*cf.* Ref. 1a).

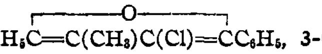
hypothesis which would apply also to the other metal derivatives described above, including the silver salts. The two reactions cited which might support such an assumption, namely, bromination and hydrolytic fission, may in our opinion be interpreted perfectly well in terms of the cyclic structures, and consequently we consider this hypothesis unsupported and unnecessary, although of course not excluded.

Experimental Part

Attempts to Synthesize 2-Hydroxy-4-methyl-2,5-diphenylfuranone-3, VI.—Two of the three attempts starting with mesaconic acid failed. In one of these we had hoped to utilize the rearrangement of an oxide, a method used successfully in the dibenzoyl and di-(trimethylbenzoyl) series. However, the substitution of methyl on the ethylene linkage of dibenzoylethylene apparently hinders the formation of an oxide to some extent under the usual conditions. At 55–60° in alcohol, hydrogen peroxide reacted with dibenzoylmethylethylene to give an intractable oil (possibly containing the oxide) which on reduction gave some dibenzoylmethylethane, but treatment with ethereal hydrogen chloride gave only non-crystalline products.

We were unable to follow the scheme used to prepare the triphenyl compound, XXII, namely, halogenation of the acetoxyfuran and subsequent hydrolysis of the chlorofuranone,[2] because dibenzoylmethylethylene under the usual conditions at room temperature failed to react with acetic anhydride and sulfuric acid, and at higher temperatures, or with more sulfuric acid, or with pyridine instead as catalyst, gave intractable products.

The steps in the successful synthesis are outlined below under the compounds involved.



$C_6H_5C{=}C(CH_3)C(Cl){=}CC_6H_5$ (ring closed through O), **3-Chloro-4-methyl-2,5-diphenylfuran.**—To an ice-cold suspension of dibenzoylmethylethylene in acetyl chloride was added 1–2 drops of concd. sulfuric acid. After five minutes (longer standing gave a poorer product) the mixture was decomposed in water and the resinous product purified by repeated crystallization from ethanol: m. p. 82–82.5° (corr.).

Anal. Calcd. for $C_{17}H_{13}OCl$: C, 76.0; H, 4.9. Found: C, 76.2; H, 5.0.

3-Bromo-4-methyl-2,5-diphenylfuran, II.—To an ice-cold suspension of 5 g. of dibenzoylmethylethylene in 25 cc. of acetic anhydride was added 10 cc. of 30% hydrogen bromide in acetic acid, and five drops of concd. sulfuric acid. After standing for fifteen minutes (the temperature being allowed to rise) it was decomposed in ice and slowly diluted with water. Usually under these conditions the crude product could be obtained crystalline; yield 5 g. It was crystallized from ethanol by cooling cautiously and seeding; m. p. 73.5° (corr.). Mixed melting points with the corresponding chloro compound (above) showed no depression.

Anal. Calcd. for $C_{17}H_{13}OBr$: C, 65.2; H, 4.2. Found: C, 65.3; H, 4.4.

1,2-Dibenzoyl-1-bromopropylene-1 (Dibenzoylbromomethylethylene), III, was obtained in good yield by oxidation of II in glacial acetic acid with concd. nitric acid according to the method of Lutz and Wilder.[8] It was crystallized from ethanol: m. p. 85° (corr.).

Anal. Calcd. for $C_{17}H_{13}O_2Br$: C, 62.0; H, 4.0. Found: C, 61.9; H, 4.1.

Reduction with zinc and glacial acetic acid at 90–100° (ten minutes) gave an oil from which dibenzoylmethylethane was isolated.

1,2-Dibenzoyl-1-methoxypropylene-1 (Dibenzoylmethoxymethylethylene), IV, was obtained as a yellow oil when a methanol solution of one equivalent each of sodium methylate and dibenzoylbromomethylethylene, III, were allowed to interact at room temperature for two hours. It was isolated by diluting the reaction mixture with water and extracting with ether. It could not be induced to crystallize and was distilled (b. p. 185–195° at 2 mm. pressure), but insufficient material was available for elaborate purification. Analyses were not good, but they approximated the assigned formula. The identity of the substance was shown by ozonization.

Ozonization of 3.6 g. in chloroform for twenty-one hours, subsequent evaporation of the solvent, and hydrolysis with water, gave an oil which was taken up in ether and extracted with sodium bicarbonate solution. On acidification of the latter 1.2 g. (about 75% of one equivalent) of benzoic acid was isolated. The non-acidic oil obtained from the ether solution was hydrolyzed with boiling aqueous potassium hydroxide, and on acidification and treatment with semicarbazide hydrochloride, gave 1.0 g. of phenylglyoxylic acid semicarbazone which was identified by mixed melting point (this corresponds to a yield of 44% of the methyl ester of phenylglyoxylic acid).

Hydrolysis of 0.4 g. of the methoxy compound, IV, in a mixture of 4 cc. of glacial acetic acid, 1 cc. of concd. hydrochloric acid, and 1 cc. of water (standing three hours at room temperature) gave a crude product from which 0.2 g. of pure hydroxymethyldiphenylfuranone, VI, was isolated and identified by mixed melting point with an authentic sample previously prepared by alkylation of diphenylbutanetrione silver enolate.

The reaction between dibenzoylbromomethylethylene, III, and sodium methylate is of interest in connection with a mechanism proposed for the similar conversion of dibenzoylbromoethylene into dibenzoylmethoxyethylene. In the latter case dibenzoylacetylene, $C_6H_5COC{\equiv}CCOC_6H_5$, was suggested as a likely intermediate since it could be isolated under other and controlled conditions, and since it undergoes the type of reaction in question with great ease.[9] In the case of dibenzoylbromomethylethylene, however, with the methyl group on the ethylene linkage, an acetylenic diketone could not form. Therefore in this case at least a different mechanism must be in-

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[8] Lutz and Wilder, This Journal, **56**, 979 (1934).

[9] Lutz, *ibid.*, **48**, 2905 (1926); Lutz, Wilder and Parrish, *ibid.*, **56**, 1980 (1934).

volved such as 1,4-addition of the reagent to the conjugated system followed by elimination of sodium bromide (direct replacement of halogen on the ethylene linkage is of course very unlikely).

2-Hydroxy-4-methyl-2,5-diphenylfuranone-3, VI, is best prepared by the action of methyl iodide on the silver derivative of diphenylbutanetrione enol according to directions already published.[1a]

Ozonization of 4 g. in chloroform for six hours (cooled in ice) gave 3.0 g. of benzoic acid (83% of two equivalents) and 0.3 g. of phenylglyoxylic acid semicarbazone (10% of one equivalent).

The sodium derivative did not crystallize from sodium alcoholate solutions (as did the sodium salt of diphenylbutanetrione enol). The hydroxyfuranone dissolves readily in the reagent, however, and does not precipitate on dilution with water. The solid sodium salt is obtained as a pale yellowish solid from ether by the direct action of metallic sodium (wire), and is quite soluble in water or alcohol. In the dry state or in solution it does not react with methyl iodide.

The silver derivative was precipitated by silver nitrate from an aqueous solution of the sodium derivative or from a solution prepared by dissolving the hydroxyfuranone in slightly less than the calculated amount of sodium methylate, diluting with water, and filtering off the undissolved material. The silver derivative was grayish-tan when first precipitated, but quickly darkened and turned black within fifteen minutes.

The results of the **K. Meyer titration,** referred to briefly in the introduction, will be given in the following paper in connection with the more general study of the reaction.

2-Methoxy-4-methyl-2,5-diphenylfuranone-3, VII, was obtained by the action of saturated methanolic hydrogen chloride (standing overnight at room temperature) on the hydroxyfuranone, VI. It crystallized from methanol or isopropyl ether; m. p. 67–68° (corr.).

Anal. Calcd. for $C_{18}H_{16}O_3$: C, 77.1; H, 5.8; OCH_3, 10.4. Found: C, 77.1; H, 5.9; OCH_3, 10.5.

The ether, VII, was obtained also according to the following schemes: (a) dropwise addition of 10% potassium hydroxide (to permanent alkalinity) to a suspension of 1 g. of the hydroxyfuranone in 50 cc. of water containing 2 cc. of dimethyl sulfate, precipitated a small amount of the methoxyfuranone, VII, as an oil. Variation in ratio of reagents, or order of addition of reagents did not improve the yield, and the bulk of the material was recovered unchanged.

(b) Two grams of the hydroxyfuranone was dissolved in 10 cc. of methanol containing 0.17 g. of dissolved sodium. After diluting with water to 75 cc. and filtering off undissolved material, 50 cc. of 2% silver nitrate solution was added, and the precipitated silver compound filtered quickly and (while still wet) treated immediately with an excess of methyl iodide. After cessation of the vigorous reaction the excess methyl iodide was evaporated and the residue worked up in the usual way. One gram of the methoxyfuranone (the sole product) was isolated and 0.2 g. of starting material was recovered.

Reactions of the Methoxyfuranone, VII.—*In dilute methanolic sodium hydroxide at room temperature,* the ether was 50% hydrolyzed to the hydroxyfuranone in two hours, and 80% hydrolyzed in this time in dilute hydrochloric–acetic acid.

The ether was recovered unchanged after six hours in a refluxing alcoholic solution of *o*-phenylenediamine.

Ozonization of 4 g., carried out in the usual way, gave 1.6 g. (91%) of benzoic acid and 65% of the calculated amount of methyl benzoate (determined by hydrolysis and isolation of 1.1 g. of benzoic acid).

2-Ethoxy-4-methyl-2,5-diphenylfuranone-3, VIII, was prepared from the hydroxyfuranone, VI, or the methoxyfuranone, VII, by the action of ethanolic hydrogen chloride, or by alcoholysis of the chlorofuranone, XI, in the usual way. It was crystallized from absolute ethanol and melted at 90–90.5° (corr.).

Anal. Calcd. for $C_{19}H_{18}O_3$: C, 77.5; H, 6.2. Found: C, 77.4; H, 6.5.

2-Chloro-4-methyl-2,5-diphenylfuranone-3, XI, was obtained in almost quantitative yield from the hydroxyfuranone, VI, by the action of acetyl chloride containing a few drops of sulfuric acid. Less satisfactory methods utilized benzoyl chloride and sulfuric acid or thionyl chloride. It was crystallized from ethyl acetate–petroleum ether combinations. It is colorless and melts at 68–69° (corr.).

Anal. Calcd. for $C_{17}H_{13}O_2Cl$: C, 71.7; H, 4.6; Cl, 12.5. Found: C, 71.5; H, 4.8; Cl, 12.7.

When heated for three minutes in ethanol with *o*-phenylenediamine it reacted completely giving the quinoxaline XIII.

2-Benzoyloxy-4-methyl-2,5-diphenylfuranone-3, X, was prepared as follows. (a) Six grams of benzoyl chloride was dropped into a well-stirred solution of 2 g. of the hydroxyfuranone in 50 cc. of 10% sodium hydroxide, and 0.2 g. of the benzoyloxyfuranone X precipitated. From the solution 1.6 g. of starting material was recovered.

(b) A suspension of 1 g. of the sodium derivative of the hydroxyfuranone (dry) in 30 cc. of isopropyl ether and 1.5 g. of benzoyl chloride was refluxed for one hour. On filtering and cooling 0.5 g. of the benzoyloxyfuranone crystallized.

(c) A mixture of 1 g. of chloromethyldiphenylfuranone, XI, 3 g. of silver benzoate (freshly precipitated from aqueous sodium benzoate by silver nitrate, and washed successively with water, ethanol and isopropyl ether), and 40 cc. of isopropyl ether was refluxed for ten hours. On filtering and cooling 0.25 g. of the benzoyloxyfuranone crystallized.

(d) A mixture of 2 g. of the hydroxyfuranone, VI, and 5 g. of benzoic anhydride, fused together at 40°, was treated with two drops of concd. sulfuric acid, allowed to stand for one hour and decomposed with sodium bicarbonate solution. The product was extracted from the residue by means of ethyl acetate and 1.9 g. obtained.

The benzoyloxyfuranone was recrystallized from ethyl acetate or isopropyl ether; it is colorless and melts at 167° (corr.).

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

Hydrolysis in sodium methylate solution (twenty minutes at room temperature) gave the hydroxyfuranone and benzoic acid.

2-Acetoxy-4-methyl-2,5-diphenylfuranone-3, IX, was prepared from the hydroxyfuranone, VI, with acetic anhydride and sulfuric acid in the usual way, and was recrystallized from ethyl acetate; m. p. 168–169° (corr.).

Anal. Calcd. for $C_{19}H_{16}O_4$: C, 74.0; H, 5.2. Found: C, 74.1; H, 5.1.

It was quickly hydrolyzed to VI by sodium methylate.

2-(α-Methylphenacyl)-3-phenylquinoxaline, XIII.—The reaction between the hydroxyfuranone, VI, and *o*-phenylenediamine in refluxing ethanol was complete in two hours and a 95% yield of the quinoxaline crystallized on cooling. It crystallized as colorless needles from ethanol, and melted at 155.5–156° (corr.).

Anal. Calcd. for $C_{23}H_{18}ON_2$: C, 81.7; H, 5.3. Found: C, 81.8; H, 5.5.

Oxidation with chromic acid in glacial acetic acid gave approximately one equivalent of benzoic acid, a 70% yield of 2-acetyl-3-phenylquinoxaline XIV, and a small amount of 2-hydroxy-3-phenylquinoxaline XV. The latter was separated by utilizing its alkali solubility. The acetylquinoxaline XIV was recrystallized from 80% ethanol and melted at 110–111°. Since Sachs and Rohmer[4b] reported the melting point as 99.5°, we analyzed our product (calcd. for $C_{16}H_{12}ON_2$: C, 77.4; H, 4.9. Found: C, 77.5; H, 5.0), converted it into the characteristic semicarbazone (m. p. 243°), and oxidized it by long refluxing in a chromic–glacial acetic acid mixture to 2-hydroxy-3-phenylquinoxaline.

2-Bis-(4-methyl-2,5-diphenyl-3-furanone), XII.—The hydroxyfuranone is not affected by sodium hydrosulfite in 80% ethanol or by stannous chloride in boiling acetic acid. Reduction with an excess of zinc dust and glacial acetic acid at 90–100° (with mechanical stirring) gave an oily product which, when taken up in ether, benzene, or dioxane, gave yields as high as 40% of the dimolecular product. Reduction of the chlorofuranone XI similarly (but at 25–35°) gave a 20% yield of XII. When shaken with hydrogen and palladium–barium sulfate catalyst in ethyl acetate, the chlorofuranone absorbed nearly one mole of hydrogen. The solvent was evaporated under a stream of nitrogen. Only oils and a 30% yield of the dimolecular compound was obtained.

The best yield of the dimolecular product was obtained by refluxing a mixture of the chlorofuranone, XI, in benzene and an excess of copper bronze. The product was crystallized from dioxane–petroleum ether mixtures, or benzene or dioxane, and melted at 283–285° (corr.).

Anal. Calcd. for $C_{34}H_{26}O_4$: C, 81.9; H, 5.3; mol. wt., 498. Found: C, 81.6; H, 5.6; mol. wt., 484.

2-Hydroxy-2,4,5-triphenylfuranone-3, XXII,[2] was obtained as colorless needles of m. p. 187–189°. It dissolved readily in 10% potassium hydroxide and was regenerated on acidification. **The silver derivative,** obtained in the usual way, was grayish-tan and darkened and turned black on standing. When freshly precipitated it reacted rapidly with methyl iodide to give the methoxyfuranone, XXIII.

3-Bromo-3-methyl-1,4-diphenyl-1,2,4-butanetrione, XVI.—The hydroxyfuranone, VI, reacts readily with one molecule of bromine in either chloroform or ethanol, the latter solvent being preferable since the bromo triketone crystallizes out directly, pure and in good yield. The bromo triketone can be obtained also from an aqueous solution of the sodium salt with one molecule of bromine. It crystallizes from ethanol, is practically colorless, but gives bright yellow solutions, and melts at 95° (corr.).

Anal. Calcd. for $C_{17}H_{13}O_3Br$: C, 59.1; H, 3.8. Found: C, 59.0; H, 3.9.

Reduction.—The bromo triketone is not affected by boiling ethanol, even after several hours of refluxing. Sodium hydrosulfite added to a boiling ethanol solution reduced it immediately. It liberated iodine from solutions of potassium iodide in glacial acetic acid or acidified ethanol, and the hydroxyfuranone, VI, was recovered from the solutions. It reacted slowly with 80% ethanol saturated with sulfur dioxide, and after three hours a good yield of the reduction product, VI, was isolated.

3-Bromo-2,2-dimethoxy-3-methyl-1,4-diphenyl-1,4-butanedione, XVII.—The acetal was obtained by the action of methanolic hydrogen chloride for twelve hours on the bromo triketone XVI. It crystallized from methanol, is colorless, and melts at 144°.

Anal. Calcd. for $C_{19}H_{19}O_4Br$: C, 58.3; H, 4.9; OCH_3, 15.87. Found: C, 58.5; 58.0; H, 5.1, 4.9; OCH_3, 15.64.

When subjected to the action of boiling glacial acetic acid containing a few drops of concd. hydrochloric acid for several minutes, it was completely hydrolyzed to the bromo triketone, XVI.

Summary

A new synthesis of 2-hydroxy-4-methyl-2,5-diphenylfuranone-3 from mesaconic acid is described. The evidence for the cyclic structure is presented. The conversions into ethers, acetate, benzoate, and chloride, are outlined, as also reduction, the quinoxaline reaction, and bromination. The reactions of the metal derivatives are contrasted with those of diphenylbutanetrione enolates. No reactions of the hypothetical open-chain enol form were observed, and the conclusion is drawn that the hydroxyfuranone form is fixed and reacts exclusively.

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