

crystallizations from (65–110°) petroleum ether, melted at 187–188°.

*Anal.* Calcd. for  $C_{25}H_{14}Cl_2$ : C, 72.95; H, 5.47. Found: C, 73.26; H, 5.92.

**Reduction of the Diketone (VI).**—The diketone (VI) (0.17 g.) was refluxed with excess zinc dust in a mixture of acetic acid (20 cc.) and water (2 cc.) for one hour. Extraction with ether gave a white solid (XIV) (0.12 g.) which, after three crystallizations from (65–110°) petroleum ether and one crystallization from a mixture of (40–60°) petroleum ether and ethanol, melted at 127–129°.

*Anal.* Calcd. for  $C_{20}H_{22}O_2$ : C, 81.63; H, 7.48. Found: C, 81.72; H, 7.50.

The glycol (XIV) when heated with freshly fused potassium bisulfate for one hour at 150–160°, gave a mixture of starting material and an uncrystallizable oil.

**Cleavage of the Glycol (XIV).**—A mixture of the glycol (XIV) (0.08 g.) and lead tetraacetate (0.15 g.) in dry benzene (5 cc.) was allowed to stand for two hours at 47° and then poured into water. Extraction with ether gave the diketone (VI) (0.013 g.)

**Monoacetate of the Diketone (VI).**—A solution of the diketone (VI) (0.49 g.) in acetic anhydride (20 cc.) was

refluxed with *p*-toluenesulfonic acid (0.2 g.) for six hours and then poured into water. Extraction with ether gave a white solid (XV) (0.13 g.) which, after four crystallizations from (65–110°) petroleum ether, melted at 123–124°.

*Anal.* Calcd. for  $C_{22}H_{22}O_3$ : C, 79.04; H, 6.59. Found: C, 79.37; H, 6.74.

Attempts to acetylate the diketone (VI) using acetic anhydride in the presence of either anhydrous potassium acetate or concentrated sulfuric acid gave either starting material or an uncrystallizable oil, respectively.

**Acknowledgment.**—The author wishes to thank Professor C. S. Marvel and other members of the staff for their advice during the course of this research.

### Summary

1. The preparation of 2,6-diphenylcyclooctandione-1,5 from bicyclo-[3,0,3]-octandione-2,6 is described.

2. The properties and reactions of 2,6-diphenylcyclooctandione-1,5 are reported.

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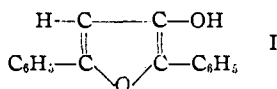
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[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY OF THE UNIVERSITY OF VIRGINIA]

## The Acylation of $\beta$ -Hydroxyfurans

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$\beta$ -Hydroxy-diphenyl (I) and triphenylfurans have been shown to exist<sup>2</sup> but they have not been isolated. As enols they both appear to react with



ferric chloride to give color, with oxygen to give peroxides, and with halogen to give 2-halogeno-3-furanones.<sup>2</sup> They appear to ketonize readily. Only one, the triphenyl derivative, has been reported in a crystalline ketonic form.<sup>2b</sup> From these facts the conclusion has been drawn<sup>2</sup> that the compounds are more like aliphatic enols than phenols. This paper deals with a study of their behavior in acylation and alkylation.

The iodomagnesium derivatives of 2,5-diphenyl-, 4-methyl-2,5-diphenyl- and 2,4,5-triphenyl- $\beta$ -hydroxyfurans were prepared by the action of methylmagnesium iodide on the corresponding  $\beta$ -acetoxyfurans. The first named of these, the diphenyl derivative (III), when treated

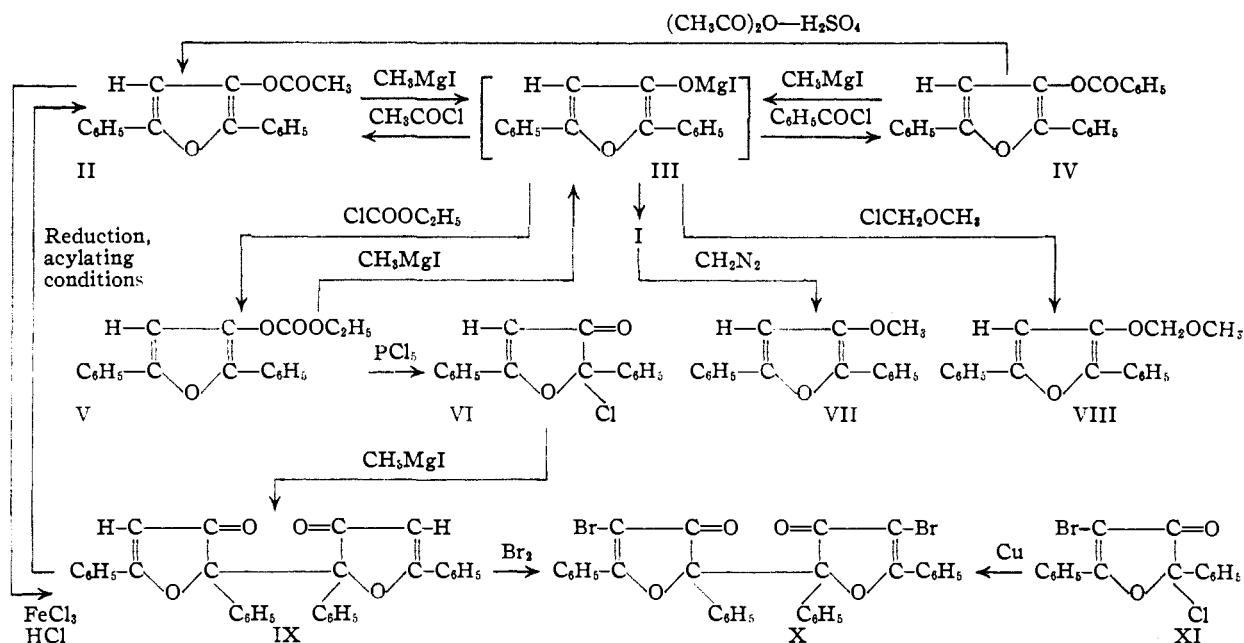
with acetyl and benzoyl chlorides, respectively, gave the acetoxyfuran (II) and the new benzoyloxyfuran (IV). The benzoyloxyfuran was converted into the acetoxyfuran (II) by the action of methylmagnesium iodide followed by treatment with acetyl chloride, a transformation which was brought about also, in one step, by the action of acetic anhydride and sulfuric acid.

The iodomagnesium derivative (III) when treated with ethyl chlorocarbonate gave the carbethoxy derivative (V). This product reacted readily with phosphorus pentachloride to give the chlorofuranone (VI). Attempts to convert it directly into the acetoxyfuran by means of acetic anhydride and sulfuric acid were unsuccessful; however, this transformation was accomplished by treatment, successively, with methylmagnesium iodide and with acetyl chloride. These reactions show that the carbethoxy compound is an oxygen-acyl derivative.

A crystalline product was obtained in the reaction with chloromethyl ether but this compound was not converted back into any one of the known derivatives mentioned above. It is presumed to be the methoxymethyl ether (VII).

(1) Present location, National Aniline Division, Allied Chemical and Dye Corp., Buffalo, N. Y.

(2) (a) Kohler, Westheimer and Tishler, *THIS JOURNAL*, **58**, 264 (1936); (b) Kohler and Woodward, *ibid.*, **58**, 1933 (1936).



Attempts to methylate the enolate (III) by means of methyl iodide and dimethyl sulfate failed. Instead of obtaining the expected methyl ether (VII) which is known, the dimolecular oxidation product (IX) was isolated in considerable amounts. The action of diazomethane on an ethereal solution of the free  $\beta$ -hydroxydiphenylfuran (I) obtained by hydrolysis of an ether solution of the iodomagnesium derivative, produced the expected methyl ether (VII) in very small yield; the bulk of the material was recovered as the dimolecular oxidation product (IX).

The oxidation of the  $\beta$ -hydroxyfuran to the dimolecular product (IX) bears analogy to the first stage in the oxidation of indoxyl to indigo, as has already been pointed out.<sup>3</sup> In this connection several experiments were suggested and carried out. One of these involved the hydrolysis of the acetoxyfuran (II) under controlled oxidizing conditions, using iodine or, better, ferric chloride, as the oxidizing agent rather than oxygen of the air. The result, as expected, was the production in good yield of the bis-furanone (IX).

A second experiment involved reduction of the bis-furanone. As was expected from the analogy to the reduction of indigo to indoxyl, reduction of the bis-furanone gave the hydroxyfuran which was isolated as the acetate (II). This reduction was accomplished in two ways. One involved catalytic hydrogen and a medium consisting of a

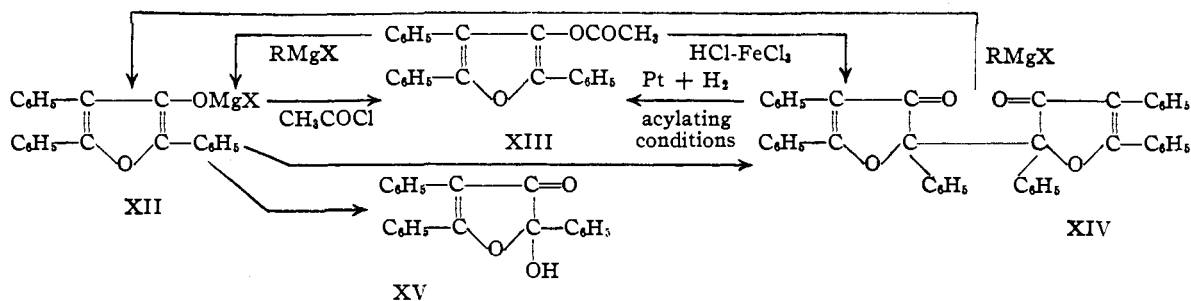
(3) Lutz and Couper, *J. Org. Chem.*, **6**, 98 (1941).

mixture of acetic acid, acetic anhydride, zinc chloride and concd. hydrochloric acid, which served to acylate the hydroxyfuran as fast as it was formed; the acetoxyfuran (II) was isolated. The other reduction of the bis-furanone was brought about through the prolonged action of the Grignard reagent followed by acylation of the resulting bromomagnesiumoxyfuran (III) with acetyl chloride. These reductions may be interpreted in terms of 1,6-addition of hydrogen or its equivalent at the oxygen atoms with simultaneous cleavage of the  $\alpha, \alpha'$ -link and generation of a double bond in each nucleus.

A third reaction of the bis-furanone was bromination. According to analogy with indigo, facile bromination of the furan or aryl nuclei would be expected; but attack at the dimolecular union would not be expected since this reagent is oxidizing in character and not reducing. Actually the expected  $\beta, \beta'$ -dibromo derivative (X) was obtained. The structure of this was demonstrated by analysis and synthesis from 4-bromo-2-chloro-2,5-diphenylfuranone (XI) through the coupling action of copper bronze.

Incidentally, description should be given here of a pertinent experiment which was carried out in a different connection.<sup>4</sup> The 2-chloro-2,5-di-

(4) In the reaction between the dimolecular oxidation product of 3-hydroxy-2,5-dimesitylfuran and the Grignard reagent, reduction occurred with the regeneration of the hydroxyfuran [Lutz and McGinn, *THIS JOURNAL*, **65**, 849 (1943)]. At first, however, this dimolecular compound had tentatively been formulated as 2-hydroxy-2,5-dimesitylfuranone-3, and the reaction with the Grignard reagent



phenyl-3-furanone (VI) underwent dimolecular reduction or coupling in the reaction with the Grignard reagent to give the bis-furanone (IX) in good yield. This reaction may be expressed also in terms of reductive enolization of the  $\alpha$ -chloro-ketone system to the magnesium enolate (II) and subsequent carbon-alkylation of this by unchanged chlorofuranone.

Attempts to duplicate the foregoing experiments in the  $\beta$ -hydroxytriphenylfuran series were only partly successful. The iodomagnesium compound (XII) was easily made but it did not react readily with acetyl or benzoyl chlorides. In the first experiments the only products isolated were the dimolecular oxidation product (XIV) and the hydroxyfuranone (XV). However, when air was excluded in a typical experiment under long treatment with acetyl chloride, the acetoxyfuran (XIII) could then be obtained in satisfactory yield.

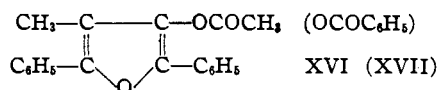
The bis-furanone (XIV), as in the case of the diphenyl analog (IX), was best obtained by hydrolysis of the acetoxyfuran (XIII) in the presence of ferric chloride as the oxidizing agent. The bis-furanone proved to be reducible by catalytic hydrogen under acylating conditions and the acetoxyfuran (XIII) was obtained in good yield. Also it was reducible slowly under the prolonged action of the Grignard reagent, the product being isolated also as the acetoxyfuran (XIII). As would be expected this bis-furanone is resistant toward the action of bromine.

The free  $\beta$ -hydroxytriphenylfuran (not isolated) did not undergo etherification with diazomethane and large amounts of the dimolecular oxidation product (XIV) were obtained (the peroxide which

consequently had been assumed to be a reductive enolization of the  $\alpha$ -hydroxyketone system [cf. Lutz and Wilder, *THIS JOURNAL*, **56**, 2065 (1934)] analogous to the 1,4-reductive enolization of an  $\alpha$ -halogenoketone [cf. Lutz and Reveley, *THIS JOURNAL*, **63**, 3180 (1941)]. We were unable to prepare for study the 2-halogeno-2,5-dimesityl-3-furanones and therefore turned to the chlorodiphenylfuranone (VI) for a test. The reductive enolization of the  $\alpha$ -hydroxyketone system of a typical hydroxyfuranone has since been demonstrated in the case of 2-*t*-butyl-2-hydroxy-4,5-diphenylfuranone-3 (Lutz and Downing, results to be published later).

might have been expected was not isolated). Evidently, steric hindrance by the  $\beta$ -phenyl group has resulted in diminution of the rates of many of the normal reactions with the consequence that dimolecular oxidation has become especially prominent.

The action of methylmagnesium iodide on acetoxydiphenylfuran (XVI) produced an iodomagnesium enolate (analogous to III) which could be converted back into the acetoxyfuran by the action of acetyl chloride. This enolate reacted also with benzoyl chloride to give the benzoyloxyfuran (XVII) which in turn could be converted back into the acetoxy compound through the iodomagnesium enolate.



The foregoing results, as far as they go, show that the  $\beta$ -hydroxyfurans behave in acylation like phenols.

### Experimental

The bromomagnesium derivative of 3-hydroxy-2,5-diphenylfuran (III) was prepared according to the directions of Kohler and Woodward<sup>2b</sup> in ether solution under an atmosphere of nitrogen.

A solution of III made from 3 g. of the acetoxyfuran (II) was added to a solution of 5 g. of acetyl chloride in 30 cc. of absolute ether. The mixture was stirred mechanically for three minutes with refluxing. After cooling and hydrolysis with 10% hydrochloric acid the ether layer was washed with 10% sodium carbonate and then with 2% hydrochloric acid. Evaporation of the ether gave a residual oil which crystallized from ethanol as colorless needles; yield 2.4 g. This was identified by mixture melting point as the acetoxyfuran (II).

Attempts to methylate with methyl iodide and with dimethyl sulfate were unsuccessful. An ether solution of III made from 3 g. of the acetoxyfuran (II) was hydrolyzed by the addition of 5% hydrochloric acid. The ether layer was separated, washed with water and dried over anhydrous sodium sulfate. This solution was cooled and added to an ice-cold ether solution of 0.8 g. of diazomethane. The mixture was allowed to come to room temperature overnight and was washed with dilute

hydrochloric acid, 10% sodium carbonate and then with water. Evaporation of the ether gave an oil from which a small amount of solid crystallized. The mixture upon digestion with isopropanol and manipulation gave a crystalline deposit of the dimolecular oxidation product (IX). Evaporation in the vacuum oven onto a cold-finger condenser, and crystallization of the distillate from ethanol gave 0.15 g. of crystals which was identified by mixture melting point as 3-methoxydiphenylfuran (VII).

**3-Benzoyloxy-2,5-diphenylfuran (IV).**—Attempts to prepare this compound by the action of benzoic anhydride and sulfuric acid on dibenzoyl ethylene were unsuccessful and led to non-crystalline products. The following procedure was developed utilizing the hydroxyfuran bromomagnesium derivative (III).

An ether solution of III made from 3 g. of the acetoxyfuran (II) was added to a solution of 6 g. of benzoyl chloride in 30 cc. of absolute ether which was precooled to 10°. A red solid separated. After refluxing for three minutes the reaction mixture was hydrolyzed in an excess of 10% hydrochloric acid and the ether layer was separated and washed in succession with dilute hydrochloric acid and sodium carbonate. The ether solution upon concentration deposited 2.4 g. (62%) of colorless needles. Recrystallization from ethanol brought the melting point to 139–140°.

*Anal.* Calcd. for  $C_{23}H_{18}O_3$ : C, 81.16; H, 4.74. Found: C, 81.31; H, 4.99.

A mixture of 0.1 g. of the benzoyloxyfuran (IV), 10 cc. of acetic anhydride and one drop of concd. sulfuric acid was allowed to stand at 25° for five minutes and was hydrolyzed in an excess of water. The product was crystallized from ethanol (yield 0.06 g.) and identified by mixture melting point as the acetoxyfuran (II).

This same transformation of IV into the acetoxyfuran (II) was accomplished in good yield by the action of methylmagnesium iodide and subsequent treatment with an excess of acetyl chloride.

**3-Carboethoxy-2,5-diphenylfuran (V).**—An ether solution of the bromomagnesium derivative (III) prepared from 3 g. of the acetoxyfuran (II) was added to a solution of 6 g. of ethyl chlorocarbonate in 25 cc. of dry ether with continuous mechanical stirring. The mixture was refluxed for five minutes, cooled and hydrolyzed with an excess of dilute hydrochloric acid. The ether layer was separated and washed twice with water. Evaporation left a red oil which was taken up in isopropanol; after standing three days 2.3 g. of stout colorless needles separated. The product was crystallized repeatedly from ethanol and melted at 66–67°.

*Anal.* Calcd. for  $C_{19}H_{16}O_4$ : C, 74.01; H, 5.23. Found: C, 73.94; H, 5.29.

A mixture of this product and 10 cc. of acetic anhydride and one drop of concd. sulfuric acid was allowed to stand for one hour at 25° and was hydrolyzed in the usual way. Starting material was recovered. At high temperatures only non-crystalline products were obtained.

Three grams of the carboethoxy derivative was added portionwise to a solution of 2.9 g. of ethylmagnesium bromide in 40 cc. of absolute ether under an atmosphere of nitrogen. The mixture was refluxed for thirty minutes, cooled, added to a solution of 6 g. of acetyl chloride in

30 cc. of absolute ether, heated under reflux for five minutes, and poured into an excess of dilute hydrochloric acid. The ether layer was washed repeatedly with dilute hydrochloric acid and with water, and evaporation gave a red oil which crystallized from ethanol; yield 2.5 g., identified by mixture melting point as the acetoxyfuran (II).

Spontaneous reaction occurred between 0.2 g. of the carboethoxy compound (V) and 0.5 g. of phosphorus pentachloride at 25°. Hydrolysis and purification of the product by crystallization from ligroin gave 0.15 g. of 2-chloro-2,5-diphenylfuranone-3 (VI) (identified by mixture melting point).

**3-(Methoxymethoxy)-2,5-diphenylfuran (VIII).**—An ethereal solution of the bromomagnesium derivative (III) prepared from 5 g. of the acetoxyfuran (II) was added to a solution of 10 g. of chloromethyl ether in 40 cc. of absolute ether. The mixture was refluxed for five minutes, cooled and hydrolyzed with an excess of 10% hydrochloric acid. The ether layer was separated, washed with water and evaporated. The residual light yellow oil crystallized from isopropanol as colorless needles (yield, 2.3 g.) and after repeated crystallization from ethanol melted at 75–75.5°.

*Anal.* Calcd. for  $C_{16}H_{16}O_3$ : C, 77.3; H, 5.8. Found: C, 77.3; H, 6.0.

Attempts to convert this compound into the acetoxyfuran (II) by acetic anhydride and a drop of concd. sulfuric acid at temperatures from 25–100° gave only non-crystalline products. The action of phosphorus pentachloride at room temperature resulted in a compound containing phosphorus (m. p. 168–169°) which has not been studied further; at 50 and 100° only non-crystalline products were obtained.

**2,2'-Bis-(2,5-diphenylfuranone-3) (IX)** has been prepared from the acetoxyfuran (II) as follows: (a) A solution of 50 g. of ferric chloride in 50 cc. of concd. hydrochloric acid was added to a solution of 25 g. of the acetoxyfuran in 200 cc. of ethanol. The mixture was refluxed for three hours, during which time crystals separated. Upon cooling, filtering and recrystallization of the product from dioxane, 10 g. of pure material was obtained; m. p. 257–259°. (b) An ether solution of 2.5 equivalents of methylmagnesium iodide was added to 0.3 g. of 2-chloro-2,5-diphenylfuranone-3 (VI) in ether. Heat was evolved. The mixture was then refluxed for five minutes and poured into a cooled solution of 3 g. of acetyl chloride in ether. A vigorous reaction occurred. The mixture was heated to boiling and hydrolyzed in an excess of ice and 10% hydrochloric acid. The ether layer was washed and evaporated and the residual oil crystallized from ethanol and identified by mixture melting point as the dimolecular compound (IX).

**Reduction of 2,2'-Bis-(2,5-diphenylfuranone-3) (IX).**—(a) **The Action of the Grignard Reagent.**—A solution of 5.5 g. of ethylmagnesium bromide and 2 g. of the bis-furanone in 50 cc. of dry ether was refluxed for one and one-half hours and allowed to stand for another one and one-half hours; the solution was then poured portionwise into a solution of 8 cc. of acetyl chloride in 30 cc. of dry ether with stirring, and under an atmosphere of dry nitrogen. After stirring for ten minutes an excess of 10%

hydrochloric acid was added slowly. When the reaction was complete, the ether layer was separated and washed in succession with sodium carbonate solution and with water. Evaporation gave an oil which crystallized from ethanol, giving 0.4 g. of the acetoxyfuran melting at 90°.

In the Kohler-Richtmyer apparatus using isoamyl ether (two check runs) the following results were obtained: active hydrogen, 0.84 and 0.80 equivalents; total methylmagnesium iodide consumed, 3.54 and 3.50 equivalents; 2.7 and 2.7 equivalents of addition.

**Catalytic Reduction.**—Hydrogenation of 1 g. of the bis-furanone in a mixture of 25 cc. of acetic anhydride, 1 g. of fused zinc chloride, 1 cc. of concd. hydrochloric acid and 0.05 g. of platinum oxide, resulted in rapid absorption of hydrogen. The reaction was interrupted after absorption of 2.5 equivalents. After filtering, the solution was poured into an excess of water. When hydrolysis appeared to be complete the mixture was neutralized with sodium carbonate and extracted with ether. Upon evaporation and treatment of the residual oil with ethanol 0.3 g. of the acetoxyfuran crystallized upon cooling.

In a separate experiment under identical conditions it was found that the acetoxyfuran absorbed hydrogen readily. Evidently the low yield in the above experiment was due to secondary reduction of the desired product.

The action of potassium iodide in concd. acetic acid was very slow at room temperature. The characteristic iodine color began to develop after several minutes and deepened on standing.

**2,2'-Bis-(4-bromo-2,5-diphenylfuranone-3) (X).**—(a) A suspension of 1 g. of the bis-furanone (IX) in 50 cc. of carbon tetrachloride was treated portionwise with 0.75 g. of bromine in 7.5 cc. of carbon tetrachloride. The mixture was refluxed for two and one-half hours and hydrogen bromide was evolved; the starting material dissolved and a new product appeared during this time. Upon cooling and filtering 0.9 g. of crude product was obtained of m. p. 275–277° (with decomposition). It was crystallized repeatedly from dioxane and showed a decomposition point between 278–280°.

*Anal.* Calcd. for  $C_{32}H_{20}Br_2O_4$ : C, 61.16; H, 3.21. Found: C, 61.42; H, 3.50.

(b) A mixture of 0.2 g. of 4-bromo-2-chloro-2,5-diphenylfuranone-3 (XI) and 0.2 g. of copper bronze in 5 cc. of dry benzene was refluxed for two and one-half hours. During this operation a crystalline precipitate appeared. The benzene was evaporated and the residue digested with 10 cc. of hot dioxane and filtered. Upon cooling 0.07 g. of colorless crystals was obtained; m. p. 266° (with decomposition). A mixture melting point with the sample from (a) showed no depression. The sample was purified further and analyzed as a check on the identification.

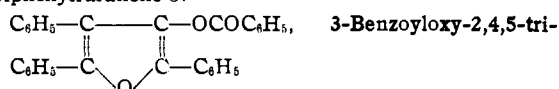
*Anal.* Calcd. for  $C_{32}H_{20}Br_2O_4$ : C, 61.16; H, 3.21. Found: C, 61.02; H, 3.65.

**3-Acetoxy-2,4,5-triphenylfuran (XIII)**<sup>2a</sup> was prepared by the addition of 1 cc. of concd. sulfuric acid to a suspension of 20 g. of dibenzoylstyrene in 100 cc. of acetic anhydride. After standing ten minutes the mixture was hydrolyzed in 800 cc. of water and the resulting solid crystallized from ethanol; yield 17 g.

The Bromomagnesium Derivative of 3-Hydroxy-2,4,5-triphenylfuran (XII) was made<sup>2a</sup> by adding 1 g. of the acetoxyfuran to 1.6 g. of ethylmagnesium bromide in 70 cc. of ether under nitrogen with refluxing for two hours.

A batch was hydrolyzed with 5% sulfuric acid and the ether layer separated and washed thoroughly, and dried with anhydrous sodium sulfate. This solution was added to 0.5 g. of diazomethane in ether solution and after standing for fifteen minutes the ether was evaporated and the residue crystallized from ethyl acetate; the yield of solid was 0.7 g.; it was identified by mixture melting point as the dimolecular oxidation product, 2,2'-bis-(2,4,5-triphenylfuranone-3).

A batch of the bromomagnesium compound was added to dimethyl sulfate in benzene; there resulted only non-crystalline products. When an ether solution of the bromomagnesium derivative was added to an ether solution of benzoyl or acetyl chloride there was obtained in each case as the only crystalline product, 2-hydroxy-2,4,5-triphenylfuranone-3.



**phenylfuran, XVIII.**—A mixture of 1 g. of dibenzoylphenylethylene and 5 g. of benzoic anhydride was fused at 50° and three drops of concd. sulfuric acid was added. The mixture was allowed to stand for one hour at 50° with occasional stirring, and was hydrolyzed in water. The resulting solid was dissolved in ethyl acetate and the solution was washed thoroughly with three portions of 10% sodium hydroxide and once with 1% hydrochloric acid. The solvent was evaporated and the residue crystallized from ethanol; yield 0.16 g., m. p. 147.5–148°.

*Anal.* Calcd. for  $C_{29}H_{20}O_3$ : C, 83.6; H, 4.84. Found: C, 83.7; H, 5.18.

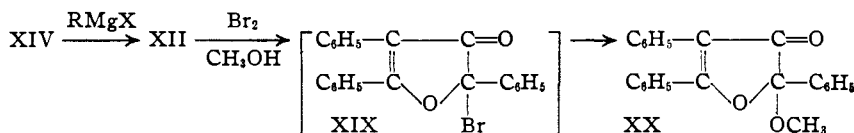
**2,2'-Bis-(2,4,5-triphenylfuranone-3) (XIV)** was prepared from the acetoxyfuran (XIII) in two ways as follows. (a) A solution of 50 g. of ferric chloride in 30 cc. of concd. acetic acid, 38 cc. of water, and 37 cc. of concd. hydrochloric acid was added to a solution of 19.5 g. of the acetoxyfuran in 100 cc. of concd. acetic acid. The mixture was refluxed for one hour and cooled; the precipitate was filtered. The solution was again refluxed for one hour, cooled and filtered; total crude yield 17 g. The product upon recrystallization from a benzene-acetone mixture weighed 12.9 g. and melted at 274–275°.

(b) A solution of 2 g. of iodine in 20 cc. of concd. acetic acid, 5 cc. of concd. hydrochloric acid and 5 cc. of water was added to a solution of 1.75 g. of the acetoxyfuran in 20 cc. of concd. acetic acid. The mixture was refluxed for 30 min. A crystalline precipitate formed rapidly. After cooling, this was filtered and washed with cold concd. acetic acid and recrystallized from a benzene-acetone mixture; yield 1.0 g.; m. p. 272–275°.

Bromine in carbon tetrachloride, under refluxing for eleven hours, was without action on the bis-furanone (XIV).

**Reduction:** (a) **The Reaction with the Grignard Reagent.**—Two grams of the bisfuranone (XIV) was treated with a large excess of ethylmagnesium bromide in 50 cc. of ether, with refluxing under an atmosphere of nitrogen

for a half hour. The mixture was added slowly over a period of thirty minutes to an excess of methanolic bromine (10 g. in 50 cc.) cooled in an ice-salt bath. The resulting mixture was poured into ice-water containing sodium bisulfite, and an excess of dilute hydrochloric acid was added. The ether layer was separated, washed and evaporated, and the residual oil was crystallized from hot ethanol. The yield of product melting at 138–140° was 0.8 g. It was identified as 2-methoxy-2,4,5-triphenylfuranone-3 (XX). In a separate experiment it was shown that the bis-furanone itself did not react with bromine under the conditions involved. The methoxyfuranone was formed presumably by methanolysis of the bromofuranone (XIX) resulting from bromination of the hydroxyfuran (XII).



(b) In a second experiment 1.5 g. of the bis-furanone was subjected to the action of a large excess of ethylmagnesium bromide (8 g. in 280 cc. of dry ether) under refluxing for a half hour. This and the succeeding operations were carried out under an atmosphere of pure nitrogen, involving a suitable device for transferring the solution to another flask under nitrogen. The solution obtained by the action of ethylmagnesium bromide on the bis-furanone was added to 10 cc. of acetyl chloride in 20 cc. of dry ether. The heat of reaction brought the mixture to boiling. The mixture was hydrolyzed by dropwise addition of 80 cc. of 4 *N* hydrochloric acid, and the ether layer was separated, washed and evaporated. The residual oil was dissolved in ethanol and gave 0.5 g. of crystals of m. p. 137–138°; this was identified as the acetoxyfuran (XIII).

(c) **Catalytic Reduction.**—A mixture of 2 g. of the bis-furanone (XIV), 2 g. of fused zinc chloride, 30 cc. of acetic anhydride, 1.5 cc. of 2 *N* hydrochloric acid, and 0.06 g. of platinum oxide was shaken under an atmosphere of hydrogen. The reaction was interrupted when one equivalent had been absorbed. The solution was filtered, poured into a large volume of water, neutralized with sodium carbonate and extracted with ether. Unchanged material remained suspended and was filtered off (1.1 g.). The ether solution upon evaporation gave an oil which was taken up in ethanol. More bis-furanone crystallized (0.2 g.). The recovered material totaled 1.3 g. and consequently 0.7 g. of the bis-furanone was used up. From the alcohol solution 0.5 g. of the acetoxyfuran (XIII) crystallized and was identified.

#### The Acylation of Bromomagnesiumoxy-triphenylfuran.

A flask was arranged with suitable devices for stirring, refluxing, introduction of reagents, protection of the reaction under an atmosphere of nitrogen, and the transfer by siphon under nitrogen to another vessel. In the first flask 4.5 g. of ethylmagnesium bromide was prepared in 60 cc. of ether. A solution of 3 g. of the acetoxyfuran (XIII) in 70 cc. of dry ether was added. After refluxing for a half hour the solution was siphoned into the second flask containing 6 cc. of acetyl chloride in 30 cc. of dry

ether. After refluxing for five minutes, 30 cc. of 10% hydrochloric acid was added dropwise. The ether layer was separated, washed and evaporated. The residual oil was dissolved in ethanol. The first crop of crystals (0.3 g.) was identified as the bis-furanone. A second crop was then obtained (0.6 g.) and identified as the acetoxyfuran (XIII).

**The Bromomagnesium Derivative of 3-Hydroxy-4-methyl-2,5-diphenylfuran.**—Three grams of the acetoxyfuran (XVI) was added portionwise to a solution of 4.3 g. of ethylmagnesium bromide in 50 cc. of absolute ether under an atmosphere of nitrogen. The mixture was refluxed for one hour and used directly.

A batch made as above was added to a solution of 6 g. of acetyl chloride in 30 cc. of dry ether. After refluxing for fifteen minutes and hydrolysis with 10% hydrochloric acid, the ether layer was separated and washed in succession with 10% hydrochloric acid, 5% sodium carbonate and with water. Evaporation of the solvent left an oil which was taken up in ligroin; 0.3 g. of the dimolecular oxidation product, 2,2'-bis-(4-methyl-2,5-diphenylfuranone-3), separated and was identified. The filtrate was evaporated and the residual oil distilled in the vacuum oven onto a cold-finger condenser. A crystalline deposit (0.2 g.) of benzoic acid came over first; then came an oil which crystallized from ethanol (1.3 g.) and was identified as the acetoxyfuran (XVI).

**3-Benzoyloxy-4-methyl-2,5-diphenylfuran (XVII).**—A batch of the bromomagnesium derivative, prepared as above, from 3 g. of the acetoxyfuran (XVI), was added to a solution of 6 g. of benzoyl chloride in 25 cc. of dry ether. The resulting mixture was refluxed for five minutes, cooled and hydrolyzed by 10% hydrochloric acid. The ether layer was separated and washed in the usual way. Evaporation left a brown oil which was distilled in the vacuum oven at 150°, and the yellow solid which collected on the cold-finger condenser was recrystallized from ethanol; pale yellow needles (0.8 g.). After repeated recrystallizations from ethanol it melted at 129.5–130°.

*Anal.* Calcd. for  $\text{C}_{24}\text{H}_{19}\text{O}_3$ : C, 81.3; H, 5.1. Found: C, 81.2; H, 5.5.

Attempts to prepare the benzoyloxy compound by the action of benzoic anhydride and concd. sulfuric acid on *cis*-dibenzoylpropylene gave only non-crystalline products.

The action of ethylmagnesium bromide on the benzoyloxyfuran (XVII) followed by addition of the resulting solution to acetyl chloride in ether, gave the acetoxyfuran (XVI) in good yield.

#### Summary

The iodomagnesium derivative of 3-hydroxy-2,5-diphenylfuran reacts with acetyl and benzoyl chlorides, with chlorocarbonic ester and with chloromethyl ether to give oxygen derivatives. It does not react normally with methyl iodide or dimethyl sulfate, but the free enol reacts with diazomethane to give the methyl ether.

A study has been made of the reactions,

particularly reduction, of the dimolecular oxidation product of the  $\beta$ -hydroxyfuran, namely,

2,2'-bis-(2,5-diphenylfuranone-3).

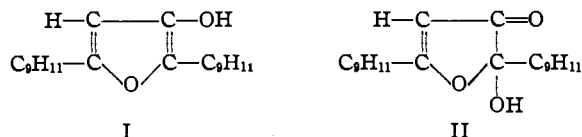
CHARLOTTESVILLE, VIRGINIA RECEIVED JANUARY 21, 1943

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

### 3-Hydroxy-2,5-dimesitylfuran and Related Compounds

BY ROBERT E. LUTZ AND C. EDWARD MCGINN<sup>1</sup>

This report deals with an attempt to prepare 2,5-dimesityl-3-hydroxyfuran (I) and 2-hydroxyfuranone-3 (II). It was anticipated that the magnesium derivative of the hydroxyfuran could be made by the action of the Grignard reagent on the acetoxyfuran (IV); however, because of steric hindrance,<sup>2</sup> it seemed unlikely that the hydroxyfuranone could be obtained by the usual methods, although it might well be stable when once formed. Evidence for the existence of the hydroxyfuran now has been obtained but the hydroxyfuranone remains as yet unknown.

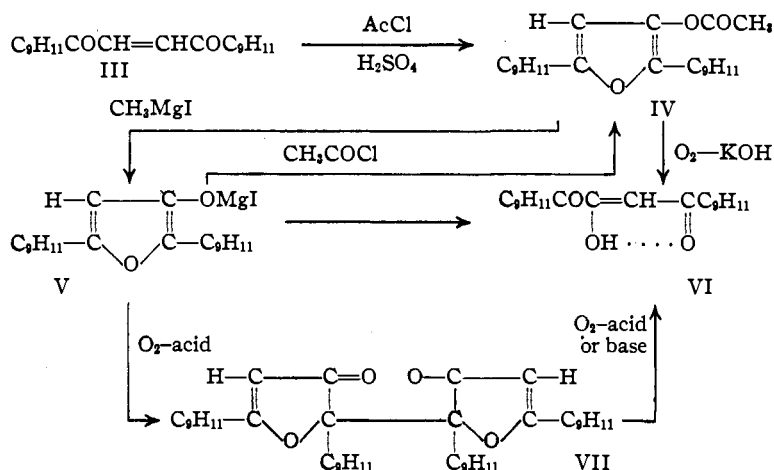


In the preparation of quantities of the acetoxyfuran (IV) by the action of acetyl chloride and

of a compound which was shown to be dimolecular ( $\text{C}_{44}\text{H}_{46}\text{O}_4$ ) and formed by hydrolysis of the acetoxyfuran and oxidation. This dimolecular compound, which is presumed to be the bis-furanone (VII), had previously been obtained by the action of concd. hydrochloric and acetic acids on the 4-hydroxy-1,4-dimesityl-1,3-butanedione 1-enol ether (IX),<sup>3</sup> but its structure was not known at that time.

The acetoxyfuran (IV) reacted with methylmagnesium iodide to give the iodomagnesium enolate (V) which could be converted back into the acetoxy compound by means of acetyl chloride. The iodomagnesium derivative reacted with benzoyl chloride to give the analogous benzoyloxy compound which in turn could be converted back into the acetate (IV) by treatment successively with the Grignard reagent and with acetyl chloride.

Unsuccessful attempts were made to isolate the



sulfuric acid on dimesityloethylene (III)<sup>3</sup> consistently high yields were obtained when special care was taken during hydrolysis of the excess of reagent to avoid hydrolysis of the acetoxyfuran itself. Otherwise there was produced large amounts

of the free hydroxyfuran (I). This compound was undoubtedly present in the non-crystalline product of hydrolysis of the iodomagnesium enolate (V) because, when this product was allowed to stand, oxygen was absorbed slowly and in time increasingly large amounts of the crystalline dimolecular oxidation product (VII) could be isolated. When the acetoxyfuran was hydrolyzed by means of alcoholic alkali, slow absorption of approximately one equivalent of oxygen was observed; but in this case the product isolated was the

triketone enol (VI), formed probably through hydrolysis to the hydroxyfuran (I), oxidation to the hydroxyfuranone (II) and finally rearrangement. The dimolecular oxidation product (VII) when suspended in an alkaline medium under the same conditions did not undergo any change and probably, therefore, was not involved in this particular

(1) Present location National Aniline Division, Allied Chemical and Dye Corp., Buffalo.

(2) Cf. Lutz and Wood, *THIS JOURNAL*, 80 (a) 229, (b) 705 (1938); (c) Lutz and Terry, *J. Org. Chem.*, 7, 274 (1942).

(3) Lutz and Terry, *ibid.*, 7, 320 (1942).