Many of these compounds have considerable local anesthetic and antispasmodic properties, the details of which will be reported later.

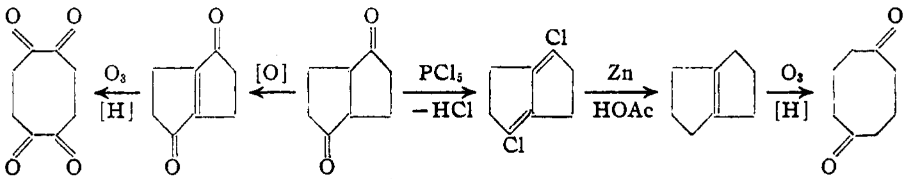
CINCINNATI, OHIO RECEIVED DECEMBER 22, 1942

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

A Synthesis of 2,6-Diphenylcycloöctandione-1,5[1a]

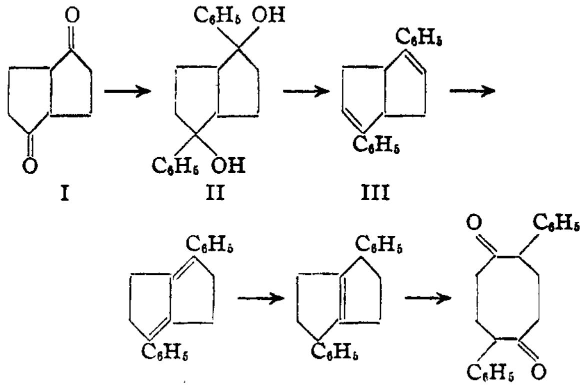
BY STANLEY WAWZONEK[1b]

The successful synthesis of *sym*-dibenzocyclooctandione-5,11 from dibenzosuccindandione-9,12[2] suggested the possibility that less substituted 1,5-diketocycloöctanes might be prepared from bicyclo-[3,0,3]-octandione-2,6 (I) by similar reactions, and subsequently used in the syntheses of cycloöctatetraenes.



(I)

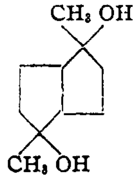
Attempts to synthesize cycloöctandione-1,5 and cycloöctantetraone-1,2,5,6 by such methods, shown below, failed because of the instability of compounds obtained in the first step in each case. The synthesis of 2,6-diphenylcycloöctandione-1,5 (VI), however, proved successful and is summarized in Formulas I-VI.



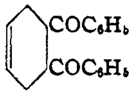
I II III

IV V VI

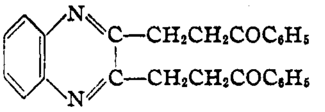
Treatment of bicyclo-[3,0,3]-octandione-2,6 (I) with phenylmagnesium bromide gave 2,6-diphenyl-2,6-dihydroxybicyclo-[3,0,3]-octane (II). The dicarbinol (II) formed chromophoric salts with mineral acids and gave a dimethyl ether when treated in methanol with a trace of sulfuric acid. Dehydration of the dicarbinol (II) with either potassium bisulfate or formic acid, gave 2,6-diphenylbicyclo-[3,0,3]-octadiene-2,6 (III). A similar dehydration when tried with 2,6-dimethyl-2,6-dihydroxybicyclo-[3,0,3]-octane (VII), obtained by adding methylmagnesium iodide to the diketone (I), gave unstable terpene-like oils. Proof for the structure of the diene (III) was its oxidation by chromic acid to 2,3-dibenzoyladipic acid. This same acid was obtained from the chromic acid oxidation of 4,5-dibenzoylcyclohexene (VIII).[3] The course of the dehydration



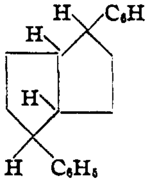
VII



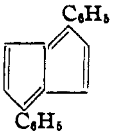
VIII



IX



X



XI

of the dicarbinol (II) indicates that the 2,6-hydroxyl groups and the 1,5-hydrogen atoms, present in this compound, must have a *cis*-configuration.

Rearrangement of the diene (III) into the higher-melting conjugated diene, 2,6-diphenylbicyclo-[3,0,3]-octadiene-1,5 (IV) was accom-

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(1a) Presented before the Division of Organic Chemistry of the American Chemical Society at the Detroit meeting, April, 1943.

(b) National Research Council Fellow, 1940–1941.

(2) Wawzonek, THIS JOURNAL, **62**, 745 (1940).

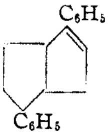
(3) Adams and Gold, *ibid.*, **62**, 56 (1940).

plished partially with some resinification by refluxing with *p*-toluenesulfonic acid in benzene. Alkaline agents such as sodium *n*-amyloxide in *n*-amyl alcohol had no effect. The structure of the conjugate diene (IV) was proved by ozonolysis. The diozonide (IVa) formed was reductively cleaved to a mixture of 1,8-diphenyloctantetraone-1,4,5,8 and β-benzoylpropionic acid. The presence of the α-diketone grouping in the tetraketone was shown by the formation of a quinoxaline (IX).

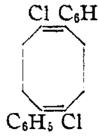
Catalytic reduction of either diene (III or IV) with platinum or palladium gave the same bicyclo-[3,0,3]-octane (X). Production of this compound from the lower melting diene (III) indicates that the 1,2,5,6- hydrogen atoms have a *cis*-configuration. Treatment of either of the dienes (III or IV) with bromine gave an amorphous powder. Such a behavior casts doubt on the possible existence of 2,6-diphenylbicyclo-[3,0,3]-octatetraene (XI), the five-membered ring analog of 1,6-diphenylnaphthalene.

Reduction of the conjugated diene (IV) in a 1,4-manner could only be accomplished with excess sodium amalgam and absolute alcohol. Other metallic combinations had no effect. The product obtained was an oil from which a solid 2,6-diphenylbicyclo-[3,0,3]-octene-(1–5) (V) could be isolated. Proof for the structure of the new hydrocarbon (V) is (1) its method of synthesis, a large excess of sodium amalgam was used in the reduction; (2) no reduction of the hydrocarbon (V) was observed at the dropping mercury electrode, a behavior pointing to an isolated double bond[4]; and (3) the hydrocarbon (V) could be rearranged by means of *p*-toluenesulfonic acid in xylene into a new hydrocarbon which was reduced at the dropping mercury electrode. The structure of the new hydrocarbon is probably XII since its half wave potential (2.57 v.) was similar to that obtained for the diene III (2.53 v.). An attempt to prepare the conjugated diene (IV) by brominating the hydrocarbon (V) and dehydrohalogenating gave a black amorphous solid. Such a behavior together with the catalytic reduction of the hydrocarbon (V) to a 2,6-diphenylbicyclo-[3,0,3]-octane, isomeric with that (X) obtained from the dienes (III, IV), indicates that the 2,6-hydrogen atoms in the hydrocarbon (V) are *trans* to each other. The residual oils from the sodium amalgam reduction could not be crystallized and were used as such in the next step.

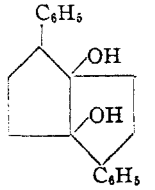
Ozonolysis of 2,6-diphenylbicyclo-[3,0,3]-octene-(1–5) (V) followed by reductive cleavage gave 2,6-diphenylcyclooöctandione-1,5 (VI). Treatment of the uncrystallizable oils from the sodium amalgam reduction in a similar manner gave a diketone (VI) with a wider melting point range. This behavior would point to a mixture of isomers. However, vacuum distillation of the product gave the higher melting diketone (VI). Apparently, the isomer present was converted by such treatment into the higher melting form.



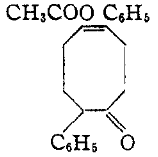
XII



XIII



XIV



XV

The presence of two carbonyl groups in the diketone (VI) was indicated by the formation of a poorly crystalline dioxime, and of a dichlorodiene (XIII) from treatment with phosphorus pentachloride in xylene. The occurrence of the 1,5-diketone grouping was shown by reduction of the diketone (VI) to a glycol (XIV) which could be cleaved back to the diketone (VI) with lead tetraacetate. Dehydration of the glycol (XIV) with potassium bisulfate gave uncrystallizable oils. The existence of the diketone (VI) in the ketonic form was indicated by its resistance to acetylation with acetic anhydride and potassium acetate. The use of acetic anhydride and *p*-toluenesulfonic acid gave a monoacetate (XV). Sulfuric acid in a similar reaction gave oils.

Experimental[5]

Bicyclo-[3,0,3]-octandione-2,6 (I).—The diketone (I) was prepared according to the directions of Ruzicka, Borges de Almeida and Brack.[6]

Treatment of the diketone (I) in benzene with phosphorus pentachloride at room temperature gave an orange-colored solution which was poured onto ice and extracted with ether. Removal of the ether under vacuum was accompanied by a blackening of the solution and gave a black amorphous precipitate.

The diketone (I) when refluxed with selenium dioxide in absolute ethanol gave an oil which resinified upon attempted vacuum distillation.

Enolization of the diketone (I) by mesitylmagnesium bromide followed by treatment with iodine in a mixture of ethanol and ether at 0°, gave an oil which yielded mesitylene and a black residue upon vacuum distillation.

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(4) Laitinen and Wawzonek, THIS JOURNAL, **64**, 1765 (1942).

(5) Melting points are not corrected.

(6) Ruzicka, Borges de Almeida and Brack, *Helv. Chim. Acta Phys.*, **17**, 183 (1934).

2,6-Diphenyl-2,6-dihydroxybicyclo-[3,0,3]-octane (II).—A solution of the diketone (I) (13.8 g.) in a mixture of benzene (50 cc.) and ether (30 cc.) was added to 0.3 mole of phenylmagnesium bromide in ether (180 cc.) and the mixture refluxed for six hours. Decomposition with ammonium chloride solution followed by steam distillation gave 21.5 g. of the crude dicarbinol (II). Crystallization twice from benzene and once from ethyl acetate gave white needles melting at 208–212° with decomposition.

Anal. Calcd. for $C_{20}H_{22}O_2$: C, 81.63; H, 7.42. Found: C, 81.74; H, 7.53.

Treatment of the dicarbinol (II) in acetic acid with either sulfuric or hydrochloric acid gave a bluish-green solution. Addition of water discharged the color of the solution.

A solution of the dicarbinol (II) (3.5 g.) in methanol (400 cc.) was treated with seven drops of concentrated sulfuric acid and allowed to stand at room temperature for twenty-four hours. Removal of the methanol under reduced pressure gave an oil which was poured into water and extracted with ether. Removal of the ether gave a brown oil from which the white dimethyl ether (0.4 g.) could be isolated. After three crystallizations from an ether-(40–60°) petroleum ether mixture and two crystallizations from (65–110°) petroleum ether, the compound melted at 174–175°.

Anal. Calcd. for $C_{22}H_{24}O_2$: C, 82.00; H, 8.08. Found: C, 81.95; H, 8.03.

2,6-Diphenylbicyclo-[3,0,3]-octadiene-2,6 (III).—A mixture of the dicarbinol (II) (5.88 g.) and freshly fused potassium bisulfate (10.88 g.) was heated for one hour at 150–160° and then treated with water. Extraction with ether gave a brown solid (III) (3.43 g.) which formed yellow needles after crystallization once from ethyl acetate and once from methanol. It melted at 136–138°.

Anal. Calcd. for $C_{20}H_{18}$: C, 93.02; H, 6.98. Found: C, 93.00; H, 7.14.

A better yield could be obtained by using formic acid as the dehydrating agent. A solution of the crude dicarbinol (II) (11.76 g.) in acetic acid (280 cc.) was boiled under reflux with 90% formic acid (100 cc.) for two hours. Addition of hot water (to aid filtration) to the refluxing mixture gave 9.1 g. of crude crystalline diene (III). Further purification was accomplished by vacuum distillation (4 mm.); yield, 7.1 g.

2,6-Dimethyl-2,6-dihydroxybicyclo-[3,0,3]-octane (VII).—A solution of the diketone (I) (5.7 g.) in benzene (50 cc.) and excess methylmagnesium iodide in ether (60 cc.) was refluxed for four hours. Decomposition with ammonium chloride solution followed by extraction with ether gave an oil from which the dicarbinol (VII) (0.83 g.) could be isolated. After two crystallizations from benzene, white prisms melting at 133–135° were obtained.

Anal. Calcd. for $C_{10}H_{18}O_2$: C, 70.59; H, 10.59. Found: C, 70.72; H, 10.44.

Treatment of the dicarbinol (VII) in acetic acid with formic acid gave a terpene-like oil which slowly turned black upon standing.

2,3-Dibenzoyladipic Acid.—A solution of the diene (III) (0.516 g.) in acetic acid (22 cc.) was heated with a mixture of chromic anhydride (0.84 g.) and sodium bisulfate (3.75 g.) in water (3 cc.) at 100° for thirty minutes. The resulting green solution was poured into water and extracted with ether. A bicarbonate extraction of the ether layer gave a white solid (0.03 g.) which after two crystallizations from a benzene–ether mixture melted at 186–188° with gas evolution.

Anal. Calcd. for $C_{20}H_{18}O_6$: C, 67.80; H, 5.08; neut. eq., 177. Found: C, 67.77; H, 5.32; neut. eq., 175, 164.

A solution of 4,5-dibenzoylcyclohexene[3] (VIII) (2.90 g.) in acetic acid (30 cc.) was heated at 100° with chromic anhydride (2.67 g.) in water (2 cc.) for thirty minutes, then poured into water and extracted with ether. Extraction of the ether layer with sodium bicarbonate solution gave 0.5 g. of 2,3-dibenzoyladipic acid melting at 189–190° with gas evolution. A mixed melting point with the acid obtained from the diene (III) showed no lowering.

2,6-Diphenylbicyclo-[3,0,3]-octadiene-1,5 (IV).—2,6-Diphenylbicyclo-[3,0,3]-octadiene-2,6 (III) (7.1 g.) was refluxed in benzene (250 cc.) with *p*-toluenesulfonic acid (1.4 g.) for thirteen hours. Removal of part of the benzene by distillation followed by cooling gave a greenish-yellow solid (3.7 g.). The solid was washed with sodium bicarbonate solution and then recrystallized twice from ethyl acetate. The yellow needles obtained melted at 188–190°. The solid obtained from the filtrate by removing the benzene completely, gave when vacuum distilled (4 mm.), 2.1 g. of the lower melting diene (III).

Anal. Calcd. for $C_{20}H_{18}$: C, 93.02; H, 6.98. Found: C, 92.84; H, 7.01.

Refluxing the diene (III) with sodium *n*-amyloxide in *n*-amyl alcohol produced no rearrangement.

Ozonolysis of the Conjugated Diene (IV).—A solution of the conjugated diene (IV) (0.52 g.) in pure ethyl acetate (100 cc.) was treated with 7% ozone at −40°. The resulting solution was treated with platinum oxide catalyst and reduced at room temperature with hydrogen at forty pounds (2.7 atm.) pressure for twelve hours. Removal of the ethyl acetate under reduced pressure gave an oil which was taken up in ether. The ether layer after extraction with sodium bicarbonate and removal of the solvent gave an oil. Addition of methanol gave the solid 1,8-diphenyloctantetraone-1,4,5,8 (0.07 g.). Four crystallizations from (65–110°) petroleum ether gave pale yellow plates melting at 110–111°.

Anal. Calcd. for $C_{20}H_{18}O_4$: C, 74.54; H, 5.59. Found: C, 74.87; H, 5.76.

The bicarbonate extract after acidification and removal of the benzoic acid by steam distillation, gave a small amount of *β*-benzoylpropionic acid. Identification was made by comparison with an authentic sample of the acid.

Removal of the ethyl acetate before the reductive cleavage gave the solid diozonide (IVa). Three crystallizations from ethyl acetate gave a white solid melting at 122–127° with gas evolution.

Anal. Calcd. for $C_{20}H_{18}O_6$: C, 67.80; H, 5.08. Found: C, 67.73; H, 5.03.

The tetraketone (0.09 g.) when refluxed with *o*-phenylenediamine (0.03 g.) in absolute ethanol (15 cc.) with a trace of acetic acid for thirty minutes gave a quinoxaline (IX) (0.08 g.). After three crystallizations from ethanol, long silky white needles were obtained melting at 166.5–167.5°.

Anal. Calcd. for $C_{26}H_{22}O_2N_2$: C, 79.19; H, 5.58. Found: C, 79.26; H, 5.79.

The Catalytic Reduction and Bromination of Dienes, III and IV.—Treatment of either diene (III or IV) (0.26 g.) in ethyl acetate (100 cc.) with hydrogen at atmospheric pressure in the presence of either platinum or palladium gave 2,6-diphenylbicyclo-[3,0,3]-octane (X) (0.11 g.). After four crystallizations from ethanol, white prisms were obtained melting at 110–112°.

Anal. Calcd. for $C_{20}H_{22}$: C, 91.60; H, 8.40. Found: C, 91.54; H, 8.56.

Treatment of either diene (III or IV) with bromine in carbon tetrachloride at 0° gave oils which lost hydrogen bromide and gave black amorphous solids.

2,6-Diphenylbicyclo-[3,0,3]-octene-(1-5) (V).—To a refluxing solution of 2,6-diphenylbicyclo-[3,0,3]-octadiene-1,5 (IV) (6.6 g.) in dry benzene (150 cc.) with 40% sodium amalgam (47.5 g.), absolute ethanol (100 cc.) was added in small portions during the course of five hours. After this time the purplish fluorescence of the conjugated diene (IV) disappeared. The resulting solution was poured into water and extracted with ether. Removal of the ether gave an oil which upon the addition of methanol and cooling, gave crystals (1.44 g.) melting at 108–111°. Crystallization twice from (40–60°) petroleum ether and once from ethanol gave white prisms melting at 115–116°.

Anal. Calcd. for $C_{20}H_{20}$: C, 92.31; H, 7.69. Found: C, 92.22; H, 7.94.

Attempts to reduce the conjugated diene (IV) using zinc and acetic acid, zinc and ammonium chloride in both ethanol and *n*-amyl alcohol, zinc and potassium hydroxide, aluminum amalgam in ethanol, and titanous chloride, were all unsuccessful. The starting material was obtained in each case. Attempts to add potassium and sodium to the conjugated diene (IV) in dibutyl ether, ether and in the dimethyl ether of ethylene glycol were likewise failures.

The residual oils obtained in the sodium amalgam reduction would not crystallize and were used as such in the ozonolysis.

Chemical Properties of 2,6-Diphenylbicyclo-[3,0,3]-octene-(1,5) (V). (a) **Catalytic Reduction.**—The hydrocarbon (V) (0.065 g.) when treated in ethyl acetate (25 cc.) with hydrogen at atmospheric pressure in the presence of platinum oxide catalyst gave a white solid (0.04 g.) melting at 95–97°. After two crystallizations from ethanol white plates were obtained melting at 99–100°. The compound when mixed with 2,6-diphenylbicyclo-[3,0,3]-octane obtained from the dienes (III, IV) gave a depression in melting point.

Anal. Calcd. for $C_{20}H_{22}$: C, 91.60; H, 8.40. Found: C, 91.51; H, 8.69.

(b) **Bromination.**—2,6-Diphenylbicyclo-[3,0,3]-octene-(1,5) (V) when treated with bromine in carbon tetrachloride at 0° lost hydrogen bromide and gave a black amorphous solid.

(c) **Behavior at the Dropping Mercury Electrode.**—The hydrocarbon (V) when investigated at the dropping mercury electrode in a 0.175 *M* tetrabutylammonium iodide, 75% dioxane solution[4] gave no reduction.

(d) **Rearrangement.**—2,6-Diphenylbicyclo-[3,0,3]-octene-(1,5) (V) (0.12 g.) was refluxed with *p*-toluenesulfonic acid (0.1 g.) in xylene (15 cc.) for forty-nine hours. The resulting bluish-green solution was poured into water and extracted with ether. Removal of the solvent under reduced pressure after washing with sodium bicarbonate solution, gave pale brown plates (0.05 g.) melting at 105–107°. After three crystallizations from ethanol, the compound melted at 106–108° and gave a lowering in melting point when mixed with the starting material.

Anal. Calcd. for $C_{20}H_{20}$: C, 92.31; H, 7.69. Found: C, 92.06; H, 7.75.

The following results were obtained in 0.175 *M* tetrabutylammonium iodide–75% dioxane solution at the dropping mercury electrode.

Compound	$\pi/2$ *vs.* S. C. E., volts	i_d, microamperes	C, millimoles/liter	i_d/C, microamperes/millimole/liter
XII	2.571	8.52	2.346	3.63
III	2.530	12.08	1.705	7.09

No rearrangement of 2,6-diphenylbicyclo-[3,0,3]-octene-(1,5) (V) could be obtained using sodium *n*-amyloxide in *n*-amyl alcohol.

2,6-Diphenylcycloöctandione-1,5 (VI).—2,6-Diphenylbicyclo-[3,0,3]-octene-(1,5) (V) (1.44 g.) in pure ethyl acetate (70 cc.) was treated with 7% ozone at −40°. The resulting solution was mixed with platinum oxide catalyst (0.1 g.) in pure ethyl acetate (70 cc.) and reduced at room temperature with hydrogen at thirty pounds (2.0 atm.) pressure for seventeen hours. Removal of the ethyl acetate under reduced pressure gave a solid and an oil which were separated by the addition of ether. The white solid (0.41 g.) thus obtained melted at 217–220°. After two crystallizations from ethyl acetate, white needles were obtained melting at 217–221°. The residual oil separated by the addition of ether gave after extraction with sodium bicarbonate solution, an additional 0.1 g. of the diketone (VI). The residual oils (3.5 g.) from the sodium amalgam reduction when ozonized and reduced catalytically, gave an additional amount (0.5 g.) of the diketone (VI) melting at 199–210°. Recrystallization from ethyl acetate did not materially change the melting point. Vacuum distillation (4 mm.) however gave the diketone (VI) melting at 217–220°. The oils and acidic products obtained in the ozonolysis were not investigated further.

Anal. Calcd. for $C_{20}H_{20}O_2$: C, 82.19; H, 6.85. Found: C, 81.96; H, 7.15.

The diketone (VI) (0.145 g.) when refluxed for ten hours in a mixture of ethanol (10 cc.), benzene (3 cc.) and water (1 cc.) with an excess of hydroxylamine hydrochloride neutralized by sodium carbonate, gave a poorly crystalline dioxime (0.095 g.). After two crystallizations from ethanol, the compound softened at 140° and then melted at 148–150°.

Anal. Calcd. for $C_{20}H_{22}O_2N_2$: C, 74.53; H, 6.83; N, 8.69. Found: C, 73.99; H, 7.13; N, 9.05.

Reaction of the Diketone (VI) with Phosphorus Pentachloride.—A solution of the diketone (VI) (0.15 g.) and phosphorus pentachloride (0.5 g.) in xylene (8 cc.) was refluxed for two hours and poured into water. Extraction with ether gave a white solid (0.04 g.) which after three crystallizations from (65–110°) petroleum ether, melted at 187–188°.

Anal. Calcd. for $C_{20}H_{14}Cl_2$: 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-diphenylcycloöctandione-1,5 from bicyclo-[3,0,3]-octandione-2,6 is described.

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

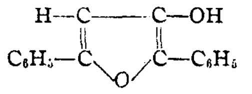
URBANA, ILLINOIS RECEIVED FEBRUARY 13, 1943

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

The Acylation of β-Hydroxyfurans

BY ROBERT E. LUTZ, C. EDWARD MCGINN[1] AND PHILIP S. BAILEY

β-Hydroxy-diphenyl (I) and triphenylfurans have been shown to exist[2] 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.[2] They appear to ketonize readily. Only one, the triphenyl derivative, has been reported in a crystalline ketonic form.[2b] From these facts the conclusion has been drawn[2] that the compounds are more like aliphatic enols than phenols. This paper deals with a study of their behavior in acylation and alkylation.



I

The iodomagnesium derivatives of 2,5-diphenyl-, 4-methyl-2,5-diphenyl- and 2,4,5-triphenyl-β-hydroxyfurans were prepared by the action of methylmagnesium iodide on the corresponding β-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 (VIII).

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[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).