

Anal. Calcd. for $C_{21}H_{18}O_6(OCH_3)$: OCH_3 , 7.91. Found: OCH_3 , 7.58.

Preparation of 3,3'-Methylenebis-(4-hydroxycoumarin) Monoethyl Ether.—The monoethyl ether was prepared by a method similar to the one described for the monomethyl ether. From the action of a hot sodium ethoxide solution on 1.3 g. of the dehydration product, 0.9 g. of the monoethyl ether, m. p. 163–166°, was obtained after two recrystallizations from ethanol.

Anal. Calcd. for $C_{21}H_{18}O_6$: C, 69.25; H, 4.40. Found: C, 69.10; H, 4.68.

Preparation of 3,3'-Ethyldenebis-(4-hydroxycoumarin) Monomethyl Ether.—Three grams of the ethylidene dehydration product was refluxed in 40 ml. of 1 *N* potassium hydroxide in methanol. The methanol insoluble salt separated out after five minutes. It was filtered off, dissolved in water, acidified and finally recrystallized twice from methanol. One gram of needles resulted, m. p. 154–155°.

Anal. Calcd. for $C_{20}H_{18}O_6(OCH_3)$: OCH_3 , 8.52. Found: OCH_3 , 8.46.

Acknowledgment.—We are indebted to our colleague, Mr. Lloyd Graf, for many of the C and H analyses reported in this paper, and to Dr. Ivan Wolff for carrying out the experiment on the dehydration with hydriodic acid and phosphorus.

Summary

1. The aldehyde condensation products of 4-hydroxycoumarin have been dehydrated to form substituted 1,4-pyran derivatives, the 3,3'-alkylidene-4,4'-epoxydicoumarins and 3,3'-arylidene-4,4'-epoxydicoumarins. This transformation was accomplished by acetic anhydride in pyridine, with all except the simplest member of the series, 3,3'-methylenebis-(4-hydroxycoumarin).

2. 3,3'-Methylenebis-(4-hydroxycoumarin) was dehydrated to the 1,4-pyran derivative by fusing with potassium acid sulfate, by heating with red phosphorus and iodine, or by treatment with diphenylphosphoric acid chloride.

3. Various monosubstituted 3,3'-methylenebis-(4-hydroxycoumarin)s yielded the dehydration product. Heating the monomethyl ether, monobenzoate, or mono-(dimethylphosphate), and treating the last two products with sodium methoxide, all yielded the dehydration product.

4. Monomethyl ethers resulted when the 1,4-pyran ring was opened by treating the dehydration products with sodium methoxide.

MADISON, WISCONSIN

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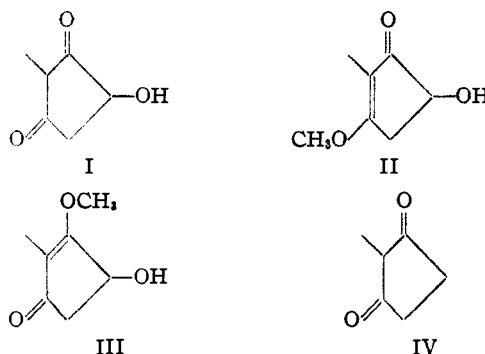
The Hydrogenation of 3-Methylcyclopentane-1,2,4-trione¹

BY MILTON ORCHIN^{1a} AND LEWIS W. BUTZ

A number of simple derivatives of methylcyclopentane, needed as intermediates in projected syntheses, are either unknown or have not been prepared by practical methods. 3-Methylcyclopentane-1,2,4-trione is readily available from 2-butanone and diethyl oxalate.² This report is concerned with the hydrogenation of the triketone in the presence of Adams catalyst at room pressure and temperature.

3-Methylcyclopentane-1,2,4-trione can be obtained anhydrous or as the monohydrate. Hydrogenation of the anhydrous triketone in ethyl acetate gave 62% of a dihydro derivative, m. p. 168°, which can be represented by formula I, although, like other 1,3-diketones with mobile hydrogen, its solutions contain enolic forms. Thus in ether it reacted with diazomethane, and two crystalline methyl derivatives, II and III, were isolated. The triketone hydrate in ethanol gave a mixture of products from which I was obtained in 39% yield and 2-methylcyclopentane-1,3-dione (IV) in 15% yield. IV has previously been obtained by the degradation of the sapo-

genin, sarcostin.³ No other products of hydrogenation were isolated.



The course of the hydrogenation is influenced by water. If traces of water are present, a small amount of 2-methylcyclopentane-1,3-dione is obtained in ethyl acetate, in addition to the hydroxy ketone. As will be shown later, the amount of hydrogen absorbed and the speed of hydrogenation were both greater in aqueous solution than in ethanol, acetic acid, or ethyl acetate. The hydroxydiketone, I, in ethanol, absorbed two moles of hydrogen very slowly. No 2-methylcyclopentane-1,3-dione could be found in the products.

(1) This work was supported by an allotment from the Special Research Fund (Bankhead-Jones Act of June 29, 1935). Not subject to copyright.

(1a) Present address: United States Bureau of Mines, Pittsburgh, Pa.

(2) Diels, Sielisch and Müller, *Ber.*, **39**, 1336 (1906).

(3) Cornforth and Earl, *J. Chem. Soc.*, 1443 (1940).

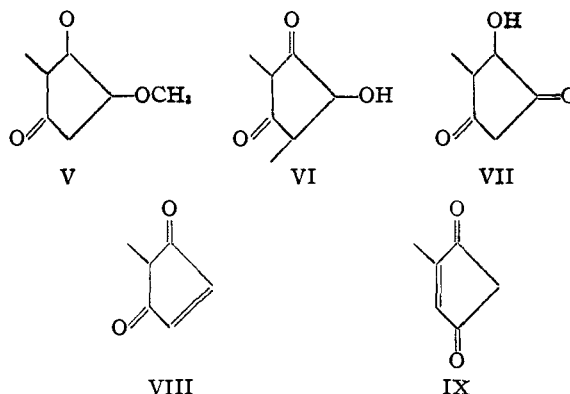
It appears that water favors the reductive elimination of one oxygen atom from the triketone and that the hydroxyketone, at least in the form isolated, is not an intermediate in the reaction. A similar case, in which sodium hydro-sulfite was the reducing agent, has been observed by Lutz and Wilder.^{3a} 1,4-Diphenylbutane-1,2,4-trione enol gave both the 2-hydroxy-1,4-diketone and the saturated 1,4-diketone—the cyclopentane compounds obtained in the present work are respectively a 4-hydroxy-1,3-diketone and a 1,3-diketone as well—and the hydroxy-diketone was not further reduced by sodium hydrosulfite. Also traces of saturated 1,4-diketone were found after catalytic hydrogenation of 1,4-dimesitylbutane-1,2,4-trione enol.^{3b}

In agreement with Cornforth and Earl, we found that 2-methylcyclopentane-1,3-dione gives a violet color with aqueous ferric chloride, yields succinic acid on oxidation with permanganate in neutral solution, and is a monobasic acid. We also found, as would be expected with a 1,3-diketone with one substituent at carbon-2, that exactly two atoms of bromine are consumed in acetic acid containing sodium acetate.⁴ In ethanol, 2-methylcyclopentane-1,3-dione shows maximal absorption at 2500 Å., ϵ 17800.⁵ 2-Ethyl-4-propylcyclopentane-1,3-dione absorbs maximally at 2550 Å., ϵ 13,200.⁶

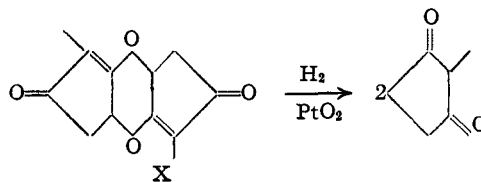
The hydroxydiketone also gave a color with ferric chloride and titrated as a monobasic acid. The two monomethyl derivatives prepared from it by reaction with diazomethane were not acidic, gave no color with ferric chloride, and were readily hydrolyzed to the original hydroxydiketone. A third crystalline monomethyl derivative was isolated in minute amount after treating the hydroxyketone with silver oxide and methyl iodide followed by dilute alkali. This compound was acidic and gave a color with ferric chloride. It may have structure V or VI.

These properties of the hydroxydiketone are consistent with either structure I or VII. However, both titration with bromine according to Voitila⁴ and the absorption maximum in the ultraviolet show that I is the correct formula. Only two atoms of bromine were consumed, whereas a compound VII, like cyclohexane-1,3-dione, should consume four atoms. In ethanol, the hydroxy ketone absorbed maximally at the same wave length, 2500 Å. (ϵ 16000), as did 2-methylcyclopentane-1,3-dione. This would be expected with the structure I, since the hydroxyl group would not influence the position of the maximum; but

a compound VII, without a methyl group at carbon-2 of the dione system, should show a maximum at shorter wave lengths than IV.



We wished to determine whether a cyclopentene-1,3-dione, VIII or IX, could be prepared by dehydration of the hydroxydiketone. This compound was recovered unchanged after heating in dilute hydrochloric acid at 80°. This resistance to dehydration, remarkable for a 3-hydroxy ketone, is probably to be attributed to the peculiar properties of the 1,3-dione system. Heating with fused potassium bisulfate at 160° gave a colorless crystalline anhydro derivative, $C_{12}H_{12}O_4$, m. p. 215°, which have 2-methylcyclopentane-1,3-dione by catalytic hydrogenation. While compounds VIII and IX might be expected to react readily with conjugated dienes, the anhydro derivative was recovered unchanged after heating with butadiene at 100° and cyclopentadiene at 125°. This behavior suggested a polymeric structure and it was then found that the substance existed as a dimer in acetic acid (m. p. 16.6°) and quinol monobenzyl ether (m. p. 121.2°). This anhydro derivative is not acidic. Of the several structures that occurred to us, X, suggested by the work of Bergmann and co-workers⁷ on 2-hydroxycyclohexanone, was the only one which seemed to be consistent with the properties. Thus the compound would be neutral and could react with hydrogen as follows



The ultraviolet absorption spectrum of the dimer supports the suggested structure X. In ethanol λ_{max} was 2520 Å., ϵ 19,000. The position of the maximum is very close to those of I and IV. Although involvement of the two enol groups in ether linkages, according to the proposed structure, would render the substance non-acidic, the

(3a) Lutz and Wilder, *THIS JOURNAL*, **55**, 2065 (1934).

(3b) Lutz and Wood, *ibid.*, **60**, 705 (1938).

(4) Voitila, *Ann. Acad. Sci. Fennicae*, **A49**, No. 1, 70 (1938).

(5) For this observation and the ultraviolet spectra for other compounds reported in this paper we are indebted to Mr. H. Bastron and Dr. R. E. Davis of this Laboratory. In a forthcoming publication the curves for these and other alicyclic polyketones will be presented, and an interesting variation of position of the maximum with concentration will be discussed.

(6) Woodward and Blout, *THIS JOURNAL*, **65**, 562 (1943).

(7) Bergmann and Giertz, *Ann.*, **448**, 48 (1926); Bergmann and Miekeley, *Ber.*, **62**, 2297 (1929).

chromophores are very similar structurally to that of the parent 1,3-dione enol.

Experimental⁸

Ethyl 4-Methyl-2,3,5-triketocyclopentylglyoxalate.^{2,9}—

To an ice cold solution of 23 g. (1 mole) of sodium in 315 cc. of absolute ethanol, there was added with good stirring and cooling a cold solution of 36 g. (0.5 mole) 2-butanone and 160 g. (1.1 moles) ethyl oxalate. The addition took about fifteen minutes and the color of the reaction mixture changed from light yellow to orange red. The mixture was allowed to come to room temperature with stirring, refluxed for half an hour (dark brown), cooled, and decomposed with 55 cc. of 1:1 sulfuric acid. The sodium sulfate was filtered and washed with ethanol; the filtrate and washings were concentrated at the water pump to about 100 cc. Strong cooling gave a precipitate which was filtered, washed with several small quantities of ice water, and allowed to dry in air. The light brown powder so obtained was dissolved in ethyl acetate, treated with norite, filtered and the filtrate concentrated; yellow needles, m. p. 160–163°, 42.9 g., sufficiently pure for conversion to the triketone.

3-Methylcyclopentane-1,2,4-trione.^{2,9}—A solution of 30 g. of ethyl 4-methyl-2,3,5-triketocyclopentylglyoxalate in 300 cc. of 1:1 phosphoric acid was refluxed half an hour, cooled to about –10°, and the precipitated oxalic acid was filtered and washed several times with small portions of ice-water. The filtrate was extracted six times with ether, the extracts were dried and evaporated, the residue was taken up in a small quantity of water, and the solution was heated with norite and filtered. On cooling 9.6 g. of long yellow needles of the monohydrate separated, m. p. 74–79°. The mother liquor yielded 1.7 g. more, m. p. 72–76°. This compound is difficult to obtain colorless, but colorless samples were separated a few times, always from the mother liquor. Anhydrous 3-methylcyclopentane-1,2,4-trione was prepared by subliming the monohydrate under reduced pressure; colorless plates, m. p. 118.2–119.6°.

4-Hydroxy-2-methylcyclopentane-1,3-dione (I).—Three grams of anhydrous triketone in 125 cc. of ethyl acetate was hydrogenated with 100 mg. of Adams catalyst. Crystals of product separated during the reaction. Absorption stopped after four hours. Ethanol was added to dissolve the precipitated product, the catalyst was filtered, and the filtrate evaporated to dryness *in vacuo*. Two crystallizations from acetone gave 1.5 g. of hydroxymethylcyclopentanedione, colorless, m. p. 166.8–168.2°. Extraction of the residue obtained on evaporating the mother liquor with ether gave 0.6 g. of triketone; yield of II on converted triketone, 62%.

*Anal.*¹⁰ Calcd. for C₆H₈O₃: C, 56.2; H, 6.3. Found: C, 56.7; H, 6.4.

2-Methylcyclopentane-1,3-dione (IV).—Sixteen grams of triketone monohydrate in 125 cc. of absolute ethanol was hydrogenated with 210 mg. of Adams catalyst. In seventy minutes, 1.52 moles of hydrogen was absorbed, and there was no further uptake after five hours; total, 1.65 moles. The catalyst was filtered, the filtrate evaporated to dryness in nitrogen at reduced pressure, the residue dissolved in 25 cc. of hot water and left to crystallize. The impure crystals, m. p. 183–192°, after two recrystallizations from water, gave 1.66 g. of I, m. p. 210.5–212.5°. Some samples melted as high as 212–214°; literature,³ m. p. 208–210°.

Anal. Calcd. for C₆H₈O₂: C, 64.3; H, 7.2. Found: C, 64.3; H, 6.9.

The dione gave a violet color with ferric chloride in water, but no color in ethanol. Neutral equivalent,

(8) All melting points are corrected. All analyses by Dr. Carl Tiedcke unless otherwise designated.

(9) We are indebted to Mr. A. M. Gaddis for assistance in this preparation.

(10) By Dr. T. S. Ma, University of Chicago.

116; calcd., 112. The neutralized solution from this titration, containing 140 mg. of IV, was concentrated, treated with norite, and filtered. Potassium permanganate (0.5 g.) was allowed to react at room temperature, norite added, and the mixture boiled and filtered. Evaporation to dryness on the steam-bath, addition of a few drops of hydrochloric acid to the residue, evaporation again, extraction of the residue with ether, evaporation of the ether extract, dissolution of the residue in water, filtration, and evaporation, gave a crystalline product, m. p. 184–185°, not depressed by mixing with authentic succinic acid.

IV, 336 mg. (3 millimoles) and 271 mg. of sodium acetate⁴ in 10 cc. of acetic acid (not quite completely dissolved) decolorized exactly 2 cc. of 3 *N* bromine in acetic acid (480 mg. or 3 milliequivalents). Two drops more of the bromine solution gave a yellow color which persisted for more than two hours.

The aqueous filtrate from the methylcyclopentanedione was taken to dryness in nitrogen at reduced pressure, and 2.7 g. of crystalline material was obtained from the residue by washing with acetone. This was nearly pure 4-hydroxy-2-methylcyclopentane-1,3-dione (I), m. p. 165–168°. The mother liquor from this was concentrated and the precipitate fractionally crystallized. In all 10.32 g. of crystalline material was obtained, from which a total of 5.53 g. of pure II (39%) and 1.87 g. of I (15.1%) was isolated.

Oximation of 2-Methylcyclopentane-1,3-dione.—To a solution of 280 mg. of I in 5 cc. of water, there were added 330 mg. of sodium carbonate in 5 cc. of water and 410 mg. of recrystallized hydroxylamine hydrochloride in 5 cc. of water. The solution was refluxed for two and a half hours, cooled and crystallized: sixty-four mg., m. p. 198° (dec.). The dioxime was not entirely pure after one recrystallization from dilute ethanol.

Anal. Calcd. for C₆H₁₀O₂N₂: N, 19.7. Found: N, 18.5.

Properties of 4-Hydroxy-2-methylcyclopentane-1,3-dione (I).—I gave a color with ferric chloride in water, but not in ethanol. Neutral equivalent: Calcd., 128.1; found, 131 (163.7 mg. in water required 9.70 cc. of 0.1286 *N* potassium hydroxide with phenolphthalein). A hundred mg. I in 5 cc. of water and 1 cc. of concentrated hydrochloric acid was heated at 75–80° for one hour. Evaporation to dryness on a steam-bath gave unchanged I.

Reaction of I with Diazomethane.—To a suspension of 0.6 g. of I in 10 cc. of ether, there was added an excess of ethereal diazomethane. The insoluble I gradually went into solution with the evolution of nitrogen. The ether was evaporated and the crystalline residue, which became oily on standing, triturated with petroleum ether. Decantation of the liquid gave 110 mg. of crystals, m. p. 163.7–167°. Recrystallization from benzene gave a I monomethyl ether, colorless needles, m. p. 167–168.2°, mixture with I, m. p. 145–155°.

Anal. Calcd. for C₇H₁₀O₃: C, 59.1; H, 7.1. Found: C, 59.4; H, 7.1.

This ether was not acid to phenolphthalein and did not give a color with either aqueous or alcoholic ferric chloride. I was obtained from the ether when 12 mg. in 2 cc. of 0.5 *N* hydrochloric acid was heated at 60° for fifteen minutes, the solution allowed to evaporate spontaneously, the residue dried, and recrystallized from acetone; m. p. 162.5–164°, mixed m. p. 163–166°. The residue also gave a violet color with aqueous ferric chloride.

The mother liquor from the 110 mg. of enol ether gave 385 mg. more of crystalline material. By fractional crystallization from benzene-petroleum ether, this was separated into 60 mg. of the ether just described and 100 mg. of another ether, colorless needles, m. p. 85–86.4°.

Anal. Calcd. for C₇H₁₀O₃: C, 59.1; H, 7.1. Found: C, 58.3; H, 7.1.

This compound was not acidic and gave no color with ferric chloride. Hydrolysis of this ether was accomplished by heating with 0.05 *N* sodium hydroxide at 80° for fifteen

minutes, allowing to stand two hours, evaporating to dryness without heat, acidifying the residue with hydrochloric acid, and again taking to dryness. Recrystallization from acetone gave I, m. p. and mixed m. p. 165–166°, violet color with ferric chloride.

Reaction of I with Methyl Iodide and Silver Oxide.—To 1 g. of I and 6.6 g. of methyl iodide in 20 cc. of absolute methanol there was added in the cold and with stirring 5.4 g. of silver oxide. The mixture was stirred while cooling with ice for fifteen minutes, then at room temperature for one hour, and finally refluxed for a half hour. The oil obtained failed to crystallize. It was dissolved in 20 cc. of ethanol, 0.5 cc. of 10% aqueous potassium hydroxide was added, the solution warmed on the steam-bath for half an hour, cooled, made acid with hydrochloric acid, and allowed to evaporate spontaneously. When only a little solvent remained the solution was transferred to a separator and extracted with ether. The ether extracts were concentrated and petroleum ether was added. The oily crystals which separated were recrystallized from benzene-petroleum ether; 20 mg., m. p. 105–110°. Three recrystallizations raised the melting point to the constant value of 110.4–111.2°.

Anal. Calcd. for $C_7H_{10}O_3$: C, 59.1; H, 7.1. Found: C, 58.9; H, 6.8.

This compound was acidic and gave a violet color with ferric chloride. It is probably 4-methoxy-2-methylcyclopentane-1,3-dione.

Catalytic Hydrogenation of I.—Hydrogenation of 108 mg. of I in 10 cc. of absolute ethanol with 20 mg. of Adams catalyst went very slowly. At the end of six hours less than a mole had been absorbed, and after a day about 1.3 moles; total uptake (three days) about 2 moles. No IV could be found in the products.

Reaction of I with Bromine.—Sixty-four mg. of I (0.5 millimole) in 2.2 cc. of acetic acid containing 46.2 mg. of sodium acetate (0.55 millimole) (I not completely dissolved) rapidly consumed 1 cc. of *N* bromine solution (0.5 milliequivalent). The end-point was sharp. Addition to the resulting solution of 0.55 millimole more sodium acetate and continued addition of *N* bromine resulted in the further, but slower (ten minutes) reaction of 0.45 milliequivalent of bromine. When a third 0.55 millimole portion of sodium acetate was then added and the addition of bromine solution continued, about 0.35 milliequivalent more of bromine reacted, one hour being required.

Thus only one hydrogen atom in the compound is rapidly substituted by bromine under the conditions. Since two atoms of bromine would be expected to enter into a molecule VII, structure I is favored. To control this point, a substance with two hydrogen atoms at the carbon between the carbonyl groups was titrated. Sixty-four mg. of cyclohexane-1,3-dione (0.57 millimole) and 94 mg. of sodium acetate (1.14 millimoles) in 2 cc. of acetic acid consumed 2.2 cc. of *N* bromine. After addition of 111 mg. of sodium acetate in 2 cc. of acetic acid to this mixture, only 0.1 cc. more *N* bromine was consumed. The calculated volume for four atoms of bromine is 2.3 cc.

Dehydration of I.—A mixture of 2.4 g. of I and 1 g. of powdered anhydrous potassium bisulfate was heated at 160° (bath) under 20 mm. pressure for one to two minutes to start the reaction. The temperature was then lowered to 150–155° and heating under 20 mm. continued for half an hour. After cooling, the cake was broken up with water, the mixture filtered, and the solid washed with water. Dissolving in ethanol, treating with norite, filtering, and crystallizing from aqueous ethanol gave 1 g. of beautiful colorless thick needles, m. p. 211.2–215°. The mother liquor gave 0.06 g. more, m. p. 211–214°. The sample for analysis was recrystallized from benzene, m. p. 213.4–215.2°.

Anal. Calcd. for $C_6H_8O_2$: C, 65.4; H, 5.5. Found: C, 65.3; H, 5.75. Molecular weight. Calcd., 110.

Found: In acetic acid, 220. In quinol monobenzyl ether (m. p. 121.2°), 213. The constant for quinol monobenzyl ether, which has not been used previously for this purpose, was determined by measuring the melting point lowering produced by 2-methylcyclohexane-1,3-dione which was assumed to be monomeric (molecular weight, 126.15) under the conditions.¹¹ A mixture of 38.5 mg. of 2-methylcyclohexane-1,3-dione and 494.5 mg. of quinol monobenzyl ether m. p. 110.5–116°. Quinol monobenzyl ether m. p. 119.3–121.2°.

$$k = \frac{126.15 \times 494.5 \times (121.2 - 116)}{38.5 \times 1000} = 8.42$$

A mixture of 28.7 mg. of anhydrohydroxymethylcyclopentanedione and 171.7 mg. of quinol monobenzyl ether had m. p. 102.8–114.6°; lowering, 6.6°.

The compound was not acid to phenolphthalein. It failed to give an oxime by the procedure used for the oxidation of 2-methylcyclopentane-1,3-dione.

Hydrogenation of the Dimeric Anhydro Derivative.—Sixty-three mg. of anhydro compound in 10 cc. of absolute ethanol was hydrogenated at atmospheric pressure with 20 mg. of Adams catalyst. Hydrogen absorption ceased after ninety minutes; 2.34 moles. The catalyst was filtered and the alcohol in the filtrate replaced with water and left to crystallize. Thirty-eight mg. of colorless compound, m. p. 210–212°, was isolated; no m. p. depression when mixed with IV; mixture with starting material, m. p. 177–192°.

Failure of the Anhydro Compound in the Diels-Alder Reaction.—(a) To 0.5 g. in 5 cc. ethanol was added 1 cc. of butadiene. The mixture was held at 50° in a sealed tube overnight. Since the compound failed to go into solution, it was filtered and the reaction repeated using (b) 2 cc. of butadiene and 5 cc. of benzene. Heating in a sealed tube at 100° for six hours gave a clear solution. On cooling the anhydro compound was recovered unchanged. (c) A mixture of 0.45 g. of anhydride, 5 cc. of dioxane, and 1 g. of freshly distilled cyclopentadiene was heated in a sealed tube for twenty hours at 125°. Four-tenths gram of unchanged substance was recovered.

The properties of the anhydro compound, $(C_6H_8O_2)_2$, are consistent with its formulation as X.

Microhydrogenations of the Triketone.—Fifty-mg. portions of the triketone were hydrogenated in water, ethanol, acetic acid, and ethyl acetate. The moles of hydrogen absorbed and the time required in minutes were, respectively: 2.7, 185; 1.7, 35; 0.8, 40; 0.9, 120. The separation of pure hydro products from the water and the acetic acid was not attempted.

Summary

2-Methylcyclopentane-1,3-dione and 4-hydroxy-2-methylcyclopentane-1,3-dione have been prepared by the catalytic hydrogenation of 3-methylcyclopentane-1,2,4-trione. The two isomeric enol methyl ethers were prepared from the hydroxydione and a third acidic methyl derivative was obtained which may be 4-methoxy-2-methylcyclopentane-1,3-dione. When heated with potassium bisulfate, the hydroxydione gave, not a methylcyclopentene-3,5-dione, but a crystalline dimer which may contain the dicyclopenta-*p*-dioxin nucleus.

BELTSVILLE, MARYLAND

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(11) Blaise and Maire, *Bull. soc. chim.*, [4] 3, 421 (1908). We are indebted to Mr. A. M. Gaddis for the preparation of this diketone by the method of Blaise and Maire and also by the methylation of cyclohexane-1,3-dione.