The chloro and bromo derivatives of the furan and the unsaturated diketone are described.

The presence of the mesityl group does not hinder typical reactions.

CHARLOTTESVILLE, VIRGINIA

The 1,4-Dimesityl-2-phenyl 1,4-Diketones

BY ROBERT E. LUTZ AND CHARLES J. KIBLER

This series of compounds has been made in order to study the effect of terminal mesityl groups on the reactions of the saturated and unsaturated 1,4-diketone systems and on the ease of furan ring closure and ring fission. Interest centers in a comparison of the reactions of this series with, first, those of di-(trimethylbenzoyl)-ethylene, I, and, second, those of dibenzoylphenylethylene, $C_6H_5COCH=C(C_6H_5)COC_6H_5$. In the case of di-(trimethylbenzoyl)-ethylene the reactions of the conjugated systems are relatively unimpaired and like those of dibenzoylethylene itself, but of course the individual carbonyl group reactivities are lowered. In the case of dibenzoylphenylethylene, as compared with dibenzoylethylene, the full conjugated system is nearly as easily reduced, one α,β-unsaturated ketone system appears to react normally with the other definitely hindered, the ethylene linkage is unreactive as also is one of the carbonyls, but furan ring closure is if anything facilitated as also is the reverse reaction, oxidative fission of the furan ring.

1,4-Dimesityl-2-phenyl-1,4-butanedione, V, has been made from di-(trimethylbenzoyl)-ethylene, I, by 1,4-addition of phenylmagnesium bromide,[1] the reaction proceeding as indicated in the diagram through the monoenolate II to the dienolate III. The proof that the excess of phenylmagnesium bromide causes the enolization of II to III rests on the hydrolysis of the product under oxidizing conditions with the formation of the unsaturated 1,4-diketone, VI, which could only have been produced by oxidation of the dienol IV.[2] The reaction between the Grignard reagent and di-(trimethylbenzoyl)-ethylene, then, can be manipulated to give good yields of the unsaturated diketone, VI. Since the nitric–acetic acid oxidation

method has proved to be useless in the case of 2,5-dimesitylfurans, this oxidation of the dienol becomes the logical preparative method.
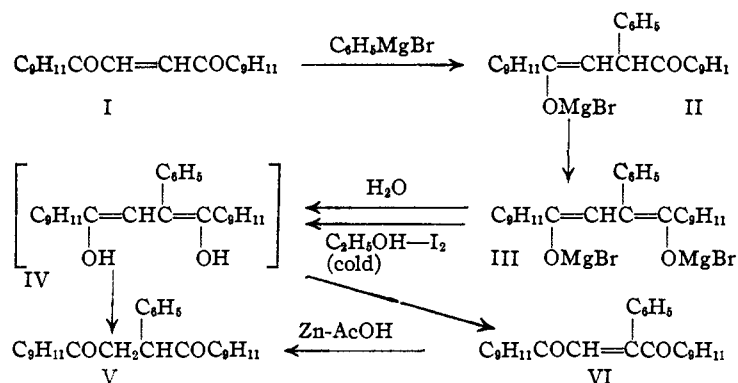
Dibenzoylphenylethylene and dibenzoylmesitylethylene, whatever the method of synthesis, appear to have the *cis* configuration with respect to the aroyl groups, and are obtainable by the oxidation both of the corresponding furans and the dienols.[2,3] It is probable, therefore, that the unsaturated diketone under discussion, VI, is also *cis*.

Reduction of the unsaturated diketone proceeds easily with zinc and acetic acid to give the saturated diketone exclusively.

Furan ring closure from the saturated diketone, V, could not be brought about by the usual procedure using acetic anhydride and sulfuric acid. Since di-(trimethylbenzoyl)-ethane itself cannot be dehydrated under these conditions,[4] it might appear that ring closure by this method is to some extent hindered by the mesityl groups; however, di - (trimethylbenzoyl) - dimethylethane, $C_9H_{11}COCH(CH_3)CH(CH_3)COC_9H_{11}$, is furanized with extraordinary ease under comparable conditions.[5] It can only be said that the 1,4-dimesityl com-

(1) Lutz and Tyson, THIS JOURNAL, **56**, 1341 (1934).

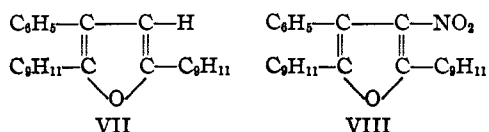(2) Lutz and Reveley, *ibid.*, **61**, 1854 (1939).

(3) (a) Lutz and Wilder, *ibid.*, **56**, 979 (1934); (b) Lutz, Tyson, Sanders and Fink, *ibid.*, **56**, 2679 (1934); (c) Lutz and Kibler, *ibid.*, **61**, 3007 (1939).

(4) Lutz, Johnson and Wood, *ibid.*, **60**, 716 (1938).

(5) Lutz and Taylor, *ibid.*, **55**, 1593 (1933).

pounds are less consistent in their behavior toward dehydrating agents than the 1,4-diketones with aryl groups which have no ortho substituents.

Furanization of the saturated diketone to VII was accomplished smoothly by the action of hydriodic acid at 150°, and also by the prolonged action of boiling acetic acid saturated continually with dry hydrogen chloride. The second of these procedures, which was only partially successful in the case of di-(trimethylbenzoyl)-ethane, proved to be very satisfactory here. It is worthy of note that the 2-phenyl group in V definitely has facilitated furan ring closure as do the 2-phenyl and 2-mesityl groups when substituted in dibenzoylethane.

$$C_6H_5-C\text{---}C-H \qquad C_6H_5-C\text{---}C-NO_2$$
$$C_9H_{11}-C \quad C-C_9H_{11} \qquad C_9H_{11}-C \quad C-C_9H_{11}$$
$$\diagdown O \diagup \qquad\qquad \diagdown O \diagup$$
$$\text{VII} \qquad\qquad\qquad \text{VIII}$$

Attempts to oxidize dimesitylphenylfuran, VII, using concentrations of the nitric–acetic acid reagent which are effective in the oxidation of various 2,5-diphenylfurans to the corresponding *cis* unsaturated 1,4-diketones, failed to open the furan ring; instead, substitution of one nitro group was the result. In view of the ease of nitration at the β-positions in dimesitylfurans and the relative unreactivity of the aryl nuclei,[6] the structure VIII has been assigned.

Attempts to convert the unsaturated diketone VI into the acetoxyfuran IX by the action of acetic anhydride or acetyl chloride and sulfuric acid failed, thus closing the door to one possible path for the preparation of the corresponding triketone enol, the synthesis of which is now being undertaken by other methods.

$$C_6H_5-C\text{---}C-OCOCH_3$$
$$C_9H_{11}-C \quad C-C_9H_{11} \qquad \text{IX}$$
$$\diagdown O \diagup$$
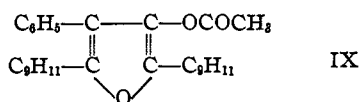
Experimental Part

2,5-Dimesityl-3-phenylfuran, VII.—Attempts to dehydrate dimesitylphenylbutanedione V with acetic anhydride and sulfuric acid under a variety of conditions from 0° to the boiling point failed. Two methods were found, the best being presented under (a).

(a) A solution of 1.0 g. of V in 25 cc. of concd. acetic acid and 1 cc. of water was refluxed gently, dry hydrogen chloride being passed through the boiling solution for thirty hours. On cooling 0.53 g. of nearly pure furan

(6) Lutz and Kibler, work on the nitration of the 2,5-dimesityl-furans, to be published shortly.

crystallized and 0.34 g. was obtained by diluting the filtrate with water and recrystallizing. It was crystallized from concd. acetic acid; rectangular plates, m. p. 104–105.5° (corr.).

Anal. Calcd. for $C_{28}H_{28}O$: C, 88.4; H, 7.4. Found: C, 88.2; H, 7.7.

(b) A mixture of 0.2 g. of V and 1 cc. of hydriodic acid (sp. gr. 1.7, protected with hypophosphorous acid) was heated in a sealed tube at 145–150° for one hour. The resinous product crystallized from ethanol giving a 74% yield of the furan.

2,5-Dimesityl-4(?)-nitro-3-phenylfuran, VIII.—A suspension of 0.1 g. of dimesitylphenylfuran, VII, in 1 cc. of concd. acetic acid, supercooled to 10°, was treated with 0.4 cc. of a 1–3 mixture of concd. nitric and acetic acids. The temperature was maintained at 10° for one hour. The product began to separate within a few minutes. Filtration gave 0.07 g. of nearly pure nitro derivative. After two crystallizations from isopropanol it separated as cubic prisms melting at 164–165° (corr.).

Anal. Calcd. for $C_{28}H_{27}O_3N$: C, 79.0; H, 6.4; N, 3.3. Found: C, 78.9; H, 6.3; N, 3.36.

1,4-Dimesityl-2-phenyl-2-butenedione-1,4, VI.—Five grams of powdered di-(trimethylbenzoyl)-ethylene, I, was added in half-gram portions to 3 equivalents of phenylmagnesium bromide in 60 cc. of absolute ether with thorough and continued mechanical stirring. The reaction was immediate and vigorous, producing a clear brown solution. This was then refluxed for a few minutes, cooled to 0°, and added slowly over ten minutes to a vigorously stirred solution of 6 g. of iodine in 200 cc. of ethanol cooled in an ice-bath. The temperature of the mixture varied between 0 and 10°. Stirring was continued for ten minutes and water containing sodium bisulfite and acidified was added to destroy the excess of iodine. Extraction with ether and subsequent concentration to small volume produced 2.9 g. of pale yellow crystals; yield 46%. Repeated crystallization from ethanol gave truncated prisms melting at 109–110° (corr.).

Anal. Calcd. for $C_{28}H_{28}O_2$: C, 84.8; H, 7.1. Found: C, 84.7; H, 7.1.

Substitution of quinone for iodine in the above oxidation produced similar results.

Reduction by means of zinc dust and boiling concd. acetic acid in the usual way produced the saturated diketone in good yield.

Attempts to convert the unsaturated diketone into the acetoxyfuran under varied conditions failed. Using acetic anhydride and concd. sulfuric acid at temperatures up to 50°, no reaction occurred, and at higher temperatures up to 100° intractable resins were obtained. Using acetyl chloride instead gave similar results but at lower temperatures from 0 to 25°.

Summary

1,4-Dimesityl-2-phenyl-2-butenedione-1,4 is made by the reaction between phenylmagnesium bromide and di-(trimethylbenzoyl)-ethylene, followed by oxidative hydrolysis of the resulting dienolate.

Dimesitylphenylfuran is made by dehydration of the saturated diketone. It is not oxidized by the nitric–acetic acid reagent.

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[Contribution from the Chemical Laboratory of The Ohio State University]

The Preparation of d- and l-Ribosidodihydroxyacetone Tetraacetates with an Orthoester Structure

By Clarence W. Klingensmith and William Lloyd Evans

In a previous communication[1] the synthesis of the first pairs of disaccharide antipodes, β-d- and β-l-arabinosidodihydroxyacetone tetraacetates and β-d- and β-l-xylosidodihydroxyacetone tetraacetates, and the synthesis of the first disaccharide racemate, β-d,β-l-arabinosidodihydroxyacetone tetraacetate were reported. In this communication another pair of antipodes containing d- and l-ribose and dihydroxyacetone is reported. The behavior of this pair of ribose derivatives as well as the synthesis of methyl-d-riboside triacetate (II) with an orthoester structure by Levene and Tipson[2] indicates that the orthoester structures, (I) and (III), should be assigned to them.
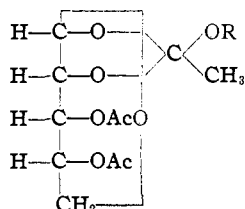
I.　R = AcOCH₂COCH₂-.　III.　R = AcOCH₂COCH₂-.
II.　R = CH₃-.
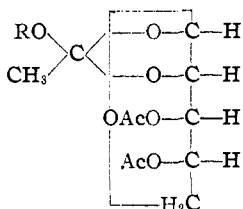
In conformity to the nomenclature proposed by Haworth, Hirst and Stacy[3] for methylglycoside acetates with an orthoester structure, our compounds are named diacetyl d-ribose-1,2-ortho-3'-acetoxyacetonyl acetate (I) and diacetyl l-ribose-1,2-ortho-3'-acetoxyacetonyl acetate (III).

Methylglycoside acetates with an orthoester structure were first obtained by Fischer, Bergmann and Rabe,[4] and the nature of their structures was first explained by Bott, Haworth and Hirst[5] and independently by Freudenberg and Scholz.[6] This type of methylglycoside acetate

has been obtained with rhamnose,[4,7] mannose,[5,8,9] lyxose,[10] maltose,[6,11] 4-[β-d-glucosido]-d-mannose,[12] ribose,[2] d-α-glucoheptose,[3] turanose,[13] fructose,[14] and talose,[15] and is characterized by (a) one acetyl group that is stable to alkaline hydrolysis and (b) extreme sensitivity to acids.

The orthoester structures of diacetyl d-ribose-1,2-ortho-3'-acetoxyacetonyl acetate and diacetyl l-ribose-1,2-ortho-3'-acetoxyacetonyl acetate differ from the orthoester structure of the methylglycoside acetates in that the acetoxyacetonyl group, AcOCH₂COCH₂-, of the former is substituted for the methyl group of the latter. The presence of the acetoxyacetonyl group made it impossible for us to demonstrate the stability of one acetyl group to alkaline hydrolysis in contrast to the removal of the other three normal acetyl groups. In an acetyl determination by the method of Kunz and Hudson,[16] diacetyl d-ribose-1,2-ortho-3'-acetoxyacetonyl acetate gave a value that was 9.4% higher than the theoretical value for four groups or 46% higher than the theoretical value for three groups. Kreider and Evans[17] previously reported that the acetyl values of oligosaccharide acetates that contained dihydroxyacetone were about 10% high by the method of Kunz and Hudson. Bernier[18] also obtained high acetyl values with dihydroxyacetone monoacetate. These high values are in accord with

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(5) H. G. Bott, W. N. Haworth and E. L. Hirst, J. Chem. Soc., 1395 (1930).

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(8) J. K. Dale, This Journal, 46, 1046 (1924).

(9) P. A. Levene and H. Sobotka, J. Biol. Chem., 67, 771 (1926).

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(11) K. Freudenberg, H. Hochstetter and H. Engels, Ber., 58, 666 (1925).

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(16) A. Kunz and C. S. Hudson, This Journal, 48, 1978 (1926).

(17) L. C. Kreider and W. L. Evans, ibid., 58, 1661 (1936).

(18) C. L. Bernier, Master's Thesis, The Ohio State University, 1933.