

The compound was recovered unchanged after several hours of refluxing with alcoholic hydrochloric acid, proving that it is not a prosapogenin. When refluxed with acetic anhydride and sodium acetate, an acetate was obtained which, after several crystallizations from aqueous methyl alcohol, melted at 102–103°; $[\alpha]^{24D} 0^\circ$; $[\alpha]^{24H\alpha} -3.5^\circ$ in dioxane.

Anal. Calcd. for $C_{27}H_{44}O_4(CH_3CO)_4$: C, 69.51; H, 9.33; acetyl, 28.48. Found: C, 69.97; H, 9.28; acetyl, 29.86, 29.52.

Summary

Bethogenin, a new sapogenin having the empirical formula $C_{27}H_{40}O_4$, has been isolated from

the hydrolysis products of extracts of powdered beth root (*Trillium erectum*). It appears to be an unsaturated steroid sapogenin with one hydroxyl group and one carbonyl group.

Another new sapogenin, trillogenin, having the empirical formula $C_{27}H_{48}O_4$, has been obtained in very small amount. This compound is saturated and is unique among the known steroid sapogenins because it lacks the two characteristic inert oxygen atoms, all four oxygen atoms being accounted for by hydroxyl groups.

STANFORD UNIV., CALIF.

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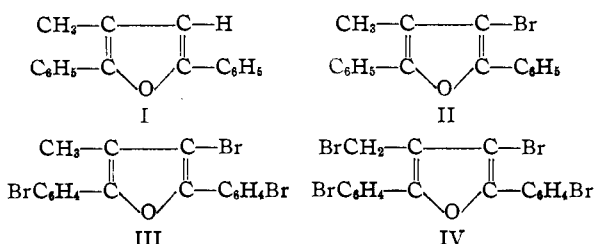
[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY OF THE UNIVERSITY OF VIRGINIA]

Halogen Compounds Derived from 4-Methyl-2,5-diphenylfuran

BY ROBERT E. LUTZ AND C. EDWARD MCGINN¹

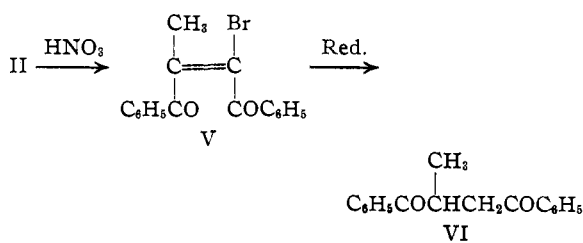
The bromination of this furan was of interest in connection with orientation² and the synthesis of certain brominated *cis* unsaturated diketones which could not easily be made otherwise.

The bromination of methyl-diphenylfuran (I) proceeded stepwise with the formation successively of the mono,³ tri and tetrabromo derivatives (II, III and IV).



Zinc and acetic acid reduced only the tetrabromo derivative and eliminated but one bromine to give the tribromo compound. The last bromine introduced therefore must have been aliphatic and located on the methyl group; and the three bromines of the tribromo compound must be aromatic. The tribromo compound on oxidation first with nitric acid and then with potassium permanganate gave more than one molecule of *p*-bromobenzoic acid, showing that two of the halogens occupied the two phenyl para positions. The remaining bromine atom, evidently the first introduced, must, therefore, be in the furan β -posi-

tion (*cf.* II). This was confirmed by nitric acid oxidation of the monobromo derivative (II) to the unsaturated bromo 1,4-diketone³ (V) and reduction of this to the saturated diketone (VI) with loss of the bromine. The structures of the three bromination products therefore are as represented in formulas II, III and IV.



Each of the three brominated furans (II, III and IV) could be oxidized by the nitric-acetic acid reagent to the corresponding unsaturated 1,4-diketones (V, VII and IX) which are presumed to be *cis* from the mode of formation. The first of these oxidation products (V) already has been reported³ The other two (VII and IX) could be converted into the saturated diketone (VIII) by reduction with zinc and acetic acid and into the furan (X) by reduction under dehydrating conditions.

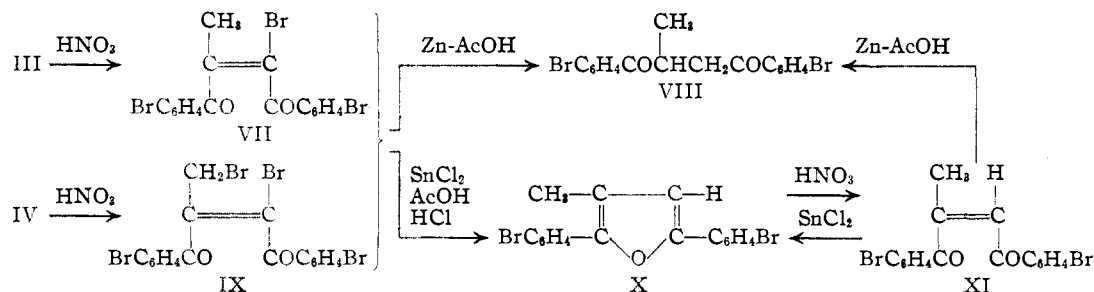
The *cis*-di-[bromobenzoyl]-propylene (XI) has become available through oxidation of the corresponding furan (X). This new unsaturated diketone in turn was reduced to the saturated diketone (VIII) and to the furan (X).

Unfortunately, it has not yet been possible to

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

(2) Lutz and Kibler, *THIS JOURNAL*, **62**, 1520 (1940).

(3) Lutz and Stuart, *ibid.*, **59**, 2316 (1937).



make any of the corresponding *trans*-compounds in this series. One important approach which should have led directly to the *trans*-isomer of XI was blocked by the failure of the Friedel-Crafts reaction between bromobenzene and mesaconyl chloride to go beyond the first stage, namely, the formation of β -bromobenzoyl- β -methylacrylic acid.⁴

Experimental

3-Methyl-2,5-di-(*p*-bromophenyl)-furan (X).—This furan was obtained in excellent yields by the stannous chloride reduction of 1-bromo-1,2-di-(*p*-bromobenzoyl)-propylene (VII), 1,2-di-(*p*-bromobenzoyl)-propylene (XI), and 1,3-dibromo-1,2-di-(*p*-bromobenzoyl)-propylene (IX). The following procedure is general.

A mixture of 30 ml. of concd. acetic acid, 25 ml. of concd. hydrochloric acid and 18 g. of stannous chloride was heated to boiling under mechanical stirring; 5 g. of (XI) in 15 ml. of concd. acetic acid was added; heating was continued for five minutes; and cooling and dilution with water gave a crystalline product. Recrystallizations from ethyl acetate raised the melting point to 158–159°. The yield of nearly pure product was 3.1 g.

Anal. Calcd. for $\text{C}_{17}\text{H}_{12}\text{Br}_2\text{O}$: C, 52.07; H, 3.09. Found: C, 52.12; H, 3.87.

3-Bromo-2,5-di-(*p*-bromophenyl)-4-methyl-furan (III). This compound was obtained directly by bromination of 3-methyl-2,5-diphenylfuran (I) by the calculated amount of bromine in chloroform solution but the method was impractical because of the difficultly separable mixture of bromination products which was obtained. The preparation is as follows:

A mixture of 2 g. of 3-bromo-4-bromomethyl-2,5-di-(*p*-bromophenyl)-furan and 2 g. of zinc dust in 70 ml. of concd. acetic acid was refluxed for five minutes and filtered. Upon dilution with water and crystallizing the resulting precipitate from a chloroform-ethanol mixture, 1.6 g. of nearly pure product (III) was obtained. Repeated crystallizations from chloroform-ethanol mixtures raised the melting point to 168–169°.

Anal. Calcd. for $\text{C}_{17}\text{H}_{11}\text{Br}_3\text{O}$: C, 43.35; H, 2.36. Found: C, 43.04, 43.03; H, 2.66, 2.66.

Zinc dust and boiling concd. acetic acid was without action on this compound.

3-Bromo-4-bromomethyl-2,5-di-(*p*-bromophenyl)-furan (IV).—A solution of 30 g. (4.1 moles) of bromine in 50 ml. of

chloroform was added to 10 g. of methyl-diphenylfuran (I) in 100 ml. of chloroform. The mixture was allowed to stand for twenty hours at room temperature, during which time hydrogen bromide was evolved, and a colorless crystalline product separated. Filtration, evaporation and finally dilution with ethanol gave successive crops totalling 17.9 g. (75%). After repeated crystallization it melted at 212–213°.

Anal. Calcd. for $\text{C}_{17}\text{H}_{10}\text{Br}_2\text{O}$: Br, 58.15. Found: Br, 58.33.

***cis*-1,4-Di-(*p*-bromophenyl)-2-methyl-2-butenedione-1,4 (XI).**—A mixture of 5 ml. of concd. nitric acid and 15 ml. of concd. acetic acid was added to a suspension of 2,5-di-(*p*-bromophenyl)-3-methylfuran (X) in 20 ml. of concd. acetic acid. After one hour at room temperature the mixture was diluted with water and the product crystallized from ethanol (yield 1.8 g.). Repeated crystallization from this solvent brought the melting point to 115–116°.

Anal. Calcd. for $\text{C}_{17}\text{H}_{12}\text{Br}_2\text{O}_2$: C, 50.0; H, 2.96. Found: C, 49.71; H, 3.08.

Sunlight was without action on a chloroform-iodine solution of this compound.

***cis*-1-Bromo-1,4-di-(*p*-bromophenyl)-2-methyl-2-butenedione-1,4 (VII).**—A mixture of 5 ml. of concd. nitric acid and 15 ml. of concd. acetic acid was added to a suspension of 5 g. of the furan (III) in 25 ml. of concd. acetic acid. After heating for one hour at 50°, diluting with ice-water and crystallizing the product from ethanol, 4.7 g. (91%) of VII was obtained. Recrystallization from ethanol brought the melting point to 119.5–120°.

Anal. Calcd. for $\text{C}_{17}\text{H}_{11}\text{Br}_3\text{O}_2$: C, 41.90; H, 2.28; Br, 49.23. Found: C, 41.46; H, 2.40; Br, 48.83.

***cis*-1-Bromo-2-(bromomethyl)-1,4-di-(*p*-bromophenyl)-2-butenedione-1,4 (IX).**—A mixture of 10 ml. of concd. nitric and 30 ml. of concd. acetic acids added to a suspension of 5 g. of IV, was heated for one hour at 50° and diluted with water. The product was crystallized from ethanol (4.5 g., 90%), and after further crystallization it melted at 117–117.5°.

Anal. Calcd. for $\text{C}_{17}\text{H}_{10}\text{Br}_4\text{O}_2$: C, 36.1; H, 1.78; Br, 56.40. Found: C, 35.77; H, 2.13; Br, 56.83.

Sunlight was without action on a chloroform-iodine solution.

1,4-Di-(*p*-bromophenyl)-2-methylbutanedione-1,4 (VIII).—The following procedure was employed using at will, VII, IX or XI.

A mixture of 5 g. of VII, 5 g. of zinc dust and 100 ml. of concd. acetic acid was refluxed for fifteen minutes, filtered and diluted with water. Extraction with ether, washing

(4) Lutz and Taylor, *THIS JOURNAL*, **55**, 1168 (1933).

the extract with water, evaporation and crystallization of the residue gave 3 g. of colorless prisms which after repeated crystallizations from ethanol melted at 120–120.5°.

Anal. Calcd. for $C_{17}H_{14}Br_2O_2$: Br, 39.0. Found: Br, 38.93.

Summary

Bromination of 3-methyl-2,5-diphenylfuran involves successive substitutions in the furan β -po-

sition, the phenyl para positions and in the methyl group.

The various brominated furans of this series have been oxidized to *cis* unsaturated diketones and these in turn have been reduced. The diketones of the di-*p*-bromophenyl series have become available through these reactions.

CHARLOTTESVILLE, VA.

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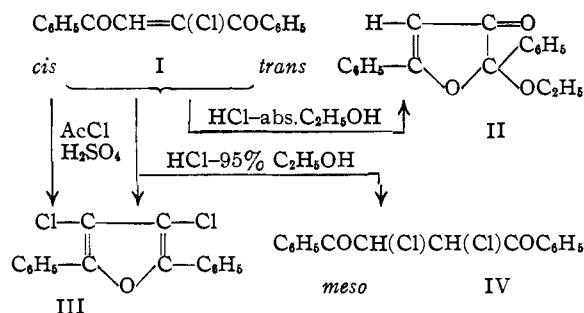
[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY OF THE UNIVERSITY OF VIRGINIA]

The Conversion of Unsaturated 1,4-Diketones into Furans and Hydroxyfuranones

BY ROBERT E. LUTZ AND C. EDWARD MCGINN¹

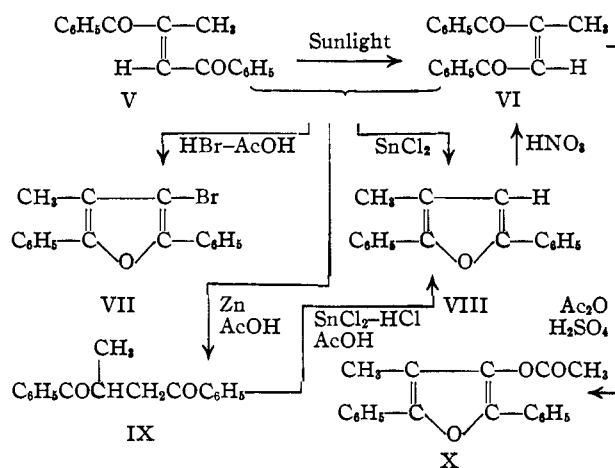
It would be expected that *cis* unsaturated 1,4-diketones would be somewhat more reactive than *trans*. This is the case with the stereoisomeric dibenzoylchloroethylenes (I) where only the *cis*-isomer reacts under the usual conditions with acetic anhydride and with acetyl chloride (with sulfuric acid as catalyst) to give, respectively, the acetoxychlorodiphenylfuran and dichlorodiphenylfuran (III).² However, both the *cis*- and *trans*-dibenzoylchloroethylenes react easily with hydrogen chloride in 95% ethanol to give the same mixture of dichlorodiketone (IV) and furan (III)³, and in absolute ethanol to give the ethoxyfuranone (II).⁴ This report deals with more reactions of these types.

Certain of the *cis* unsaturated diketones which have been difficult if not impossible to



make from the *trans*-isomers by the sunlight inversion can now be made in good yield through the corresponding furan by oxidation by means of nitric acid. This method has been applied suc-

cessfully in the preparation in quantity of *cis*-dibenzoylmethylethylene (VI) as is outlined in the diagram.



The *cis*- and *trans*-dibenzoylmethylethylenes (VI and V) are converted readily into the bromofuran (VII) by hydrogen bromide in acetic acid, but it has not been possible under the experimental conditions to determine the relative ease of reaction in the two cases. In the reaction with acetic anhydride and sulfuric acid at room temperature, on the other hand, the *trans*-compound did not react whereas the *cis*-isomer was converted in good yield into the acetoxyfuran (X). Similarly the *trans*-compound did not react with benzoic anhydride and sulfuric acid whereas the *cis*-isomer did (although, unfortunately, not to give a crystalline product). Incidentally, it has since been found that in the medium acetic anhydride, acetic acid and zinc chloride, *trans*-dimesityloethylene is reduced catalytically to the saturated diketone in the normal fashion whereas the *cis*-isomer in-

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

(2) Lutz, Stuart, Wilder and Connor, *THIS JOURNAL*, **59**, 2314 (1937).

(3) Lutz and Wilder, *ibid.*, **56**, 1193 (1934).

(4) Lutz, Wilder and Parrish, *ibid.*, **56**, 1980 (1934).