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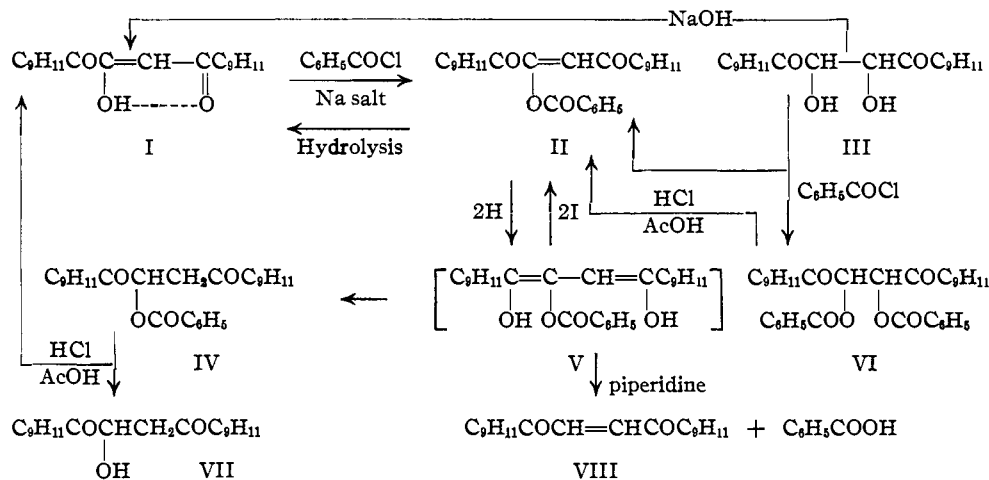
## The Acylation of 1,4-Dimesityl-1,2,4-butanetrione Enol

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Because of the variety of compounds obtained upon benzylation of diphenylbutanetrione enolate,<sup>2</sup> it became of interest to study the acylation of the dimesityl analog (I). Alkylation of the silver salts in the two cases has given different results, largely carbon-alkylation in the case of the diphenyl compound<sup>2b</sup> and oxygen-alkylation in the case of the dimesityl compound (I).<sup>3</sup> In view of these results it seemed likely that a similar difference in the behavior of the two enols would be observed in acylation and that the dimesityl compound would undergo largely oxygen-acylation, and this probably at the 4- rather than the 2-oxygen. Except for the choice of the oxygen to be involved, expectation was realized.

(III) is stable once it is formed and it therefore cannot, in this experiment, have been the precursor of the enol benzoate. This preparation of the enol benzoate from the glycol may have involved one of two paths, (a) dehydration of the glycol directly to the enol (I) followed by benzylation, or (b) formation of an unstable stereoisomeric glycol dibenzoate followed by elimination of a molecule of benzoic acid. Since path (a) is not eliminated as a possibility and path (b) has not been established, there is nothing in this preparation to show the location of the benzoyl group in the final product.

Upon further experimentation a way was found to convert the glycol dibenzoate (VI) into the



Benzylation of the sodium or silver enolate under a variety of conditions gave the bright yellow 2-enol benzoate (II) in varying yields. The best yield (60%) was obtained by the action of benzoyl chloride on the sodium enolate in dry isopropyl ether. This enol benzoate has already been described<sup>4</sup> and has been obtained by the direct action of benzoyl chloride on the free enol and also on 1,2-dimesitylglycol.

The dimesityl glycol dibenzoate (VI) which is formed along with the enol benzoate (II) in the reaction between benzoyl chloride and the glycol

enol benzoate (II) by partial hydrolysis with hydrochloric and acetic acids. There can be no question that under these circumstances the benzoyl group of the enol benzoate is one of those originally present in the glycol dibenzoate and therefore must be on the 2-oxygen in the final product.

Catalytic reduction of the enol benzoate showed absorption of one molecule of hydrogen and gave a metastable di-enol (V, not isolated) the presence of which was shown by iodine-oxidation back to the enol benzoate. We had hoped that addition of piperidine would facilitate rearrangement of this di-enol to the benzoyloxy saturated diketone (IV), but there was produced instead dimesityloethylene (VIII) and benzoic acid. However, on standing

(1) Du Pont Fellow, 1939-1940; present location, Jackson Laboratory, du Pont de Nemours Co., Wilmington, Del.

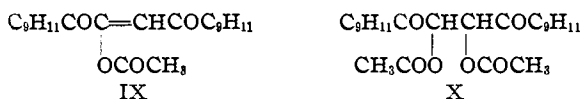
(2) (a) Lutz and Smith, *THIS JOURNAL*, **61**, 1465 (1939); (b) Lutz and Stuart, *ibid.*, **58**, 1885 (1936).

(3) Lutz and Terry, *J. Org. Chem.*, **64**, in press (1942).

(4) Fuson, McBurney and Holland, *ibid.*, **61**, 3246 (1939).

the di-enol underwent spontaneous rearrangement to the benzoyloxy saturated diketone (IV) which could then be hydrolyzed to the known hydroxy saturated diketone<sup>5</sup> (VII); also in this hydrolysis some oxidation to the triketone enol (I) occurred as might have been expected. The relationship between the enol benzoate and the hydroxy saturated diketone demonstrated in another way the structure of the enol benzoate (II).

The reactions described above have been partially duplicated in the case of the enol acetate (IX). This enol acetate was first made by the action of sodium acetate on the dibromide of dimesityloethylene,<sup>5b</sup> and we have made it also by direct acylation of the enol, by acylation of the sodium salt, and by partial hydrolysis of the 1,2-dimesitylglycol diacetate (X). The structure has already been demonstrated.<sup>5b</sup> Hydrolysis of either the enol acetate or the glycol diacetate gave the enol (I).



The foregoing results show that the sodium enolate of dimesitylbutanetrione undergoes chiefly oxygen acylation at the 2-oxygen. These results are to be contrasted with those in the benzoylation of the diphenyl analog where both the 2- and the 4-enol benzoates and also the carbon-benzoyl derivatives were obtained.

### Experimental

**1,4-Dimesitylbutane-1,2,4-trione 2-Enol Benzoate (II).**—Benzoyl chloride (1.5 g.) was added dropwise with mechanized stirring to a suspension of 3 g. of the sodium enolate of I in 50 cc. of dry isopropyl ether. The mixture was then refluxed for four hours. The precipitated sodium chloride was removed by filtration and the solvent was evaporated under reduced pressure. The residue crystallized from ethanol in a yield of 2.25 g. (60%); m. p. 139–140°; the color was bright yellow.

In a similar experiment substituting the silver enolate of I the yield of pure benzoate was 41%.

In another experiment in which the sodium enolate was suspended in aqueous 10% sodium hydroxide and treated with benzoyl chloride at room temperature with stirring, the yield of the benzoate (II) was only 24%; and the remainder of the material was recovered as the enol (I).

Upon repeated crystallization from ethanol the benzoate was obtained as yellow prisms of m. p. 141–141.5° (*cf.* ref. 4).

*Anal.* Calcd. for  $\text{C}_{29}\text{H}_{22}\text{O}_4$ : C, 79.1; H, 6.36. Found: C, 78.9; H, 6.4.

**Acid hydrolysis** of 0.7 g. of II in 25 cc. of concd. acetic acid, 6 cc. of concd. hydrochloric acid and 3 cc. of water (refluxing for fifteen minutes) gave 0.52 g. of the enol (I). **Alkaline hydrolysis** in methanol at room temperature proceeded in the same way.

**Catalytic reduction** of 1 g. of II in ethanol with 0.07 g. of platinum oxide involved absorption of one molecule of hydrogen. Two drops of piperidine was added (under hydrogen) and the mixture was allowed to stand for ten hours. Upon filtering and evaporating 0.49 g. (65%) of dimesityloethylene (VIII) was obtained and identified. From the filtrates 0.1 g. of benzoic acid was isolated.

In a similar reduction of 0.5 g. of II the resulting mixture was poured into an ethanol solution of 2 g. of iodine. Upon diluting and treating with sodium bisulfite solution, 0.32 g. of the enol benzoate was recovered.

**Ozonization** of 3 g. of II in 15 cc. of dry chloroform at 0° for eight hours was followed by evaporation of the solvent under reduced pressure and digestion of the residue with sodium bicarbonate solution. Ether extraction removed a large amount of non-acidic material which was subjected to another ozonization for ten hours, and worked up as above. The non-acidic material then was negligible and was discarded. The combined sodium bicarbonate solution was acidified and 1.87 g. of crystalline product separated. By a series of extractions and fractional distillations in the vacuum oven this material was separated into 0.57 g. (43%) of mesitylglyoxylic acid of m. p. 114–115°, 0.43 g. (56%) of benzoic acid of m. p. 116–118°, and 0.35 g. (31%) of mesitoic acid of m. p. 140–145°. These samples were purified further and identified by mixture melting points.

**2-Benzoyloxy-1,4-dimesitylbutanedione-1,4 (IV).**—Upon hydrogenation of 1 g. of the enol benzoate (II) in 40 cc. of ethanol with platinum oxide catalyst one molecule was absorbed. The mixture was then allowed to stand under hydrogen for twenty-four hours. After filtering and concentrating the solution by means of an air stream 0.4 g. (40%) of nearly pure product was obtained. Repeated crystallizations from ethanol brought the melting point to 153.5–154°. The second fraction on standing in contact with air, became yellow and 0.3 g. of the enol benzoate was then recovered.

*Anal.* Calcd. for  $\text{C}_{29}\text{H}_{30}\text{O}_4$ : C, 78.7; H, 6.77. Found: C, 78.7; H, 6.57.

**Acid hydrolysis** of 0.15 g. in 15 cc. of concd. acetic acid, 2.5 cc. of concd. hydrochloric acid and 2 cc. of water (refluxed for one and one-half hours) gave 0.02 g. of unchanged material and 0.1 g. of a mixture which was shown to contain about equal amounts of the triketone enol (I) and the hydroxy-1,4-diketone (VII).

The compound (IV) remained unchanged after heating for one hour in the vacuum oven at 180–190° under 40 mm. pressure.

**2,3-Dibenzoyloxy-1,4-dimesitylbutanedione-1,4 (1,2-Dimesitylglycol Dibenzoate) (VI).**—A solution of 2 g. of the glycol (III), prepared according to directions developed for the triethylphenyl analog<sup>4</sup> in 10 cc. of benzoyl chloride was refluxed for six hours. Upon hydrolysis and extraction of the non-acidic material with ether, 1.4 g. of crude solid product was obtained. Repeated crystallizations from ethanol raised the melting point to 162°.

*Anal.* Calcd. for  $C_{26}H_{34}O_6$ : C, 76.87; H, 6.05. Found: C, 76.63; H, 6.06.

From the filtrates from the above purification, a yellow solid was obtained which after repeated crystallizations from ethanol melted at 141–142.5° and was identified by mixture melting point as the enol benzoate (II).

A solution of 0.11 g. of the dibenzoate (VI) in 5 cc. of benzoyl chloride was refluxed for six hours and worked up as above; 0.09 g. was recovered, together with 0.01 g. of a brownish-orange solid melting at 180–182° which was not identified or studied further.

**Acid hydrolysis** of 0.5 g. of the dibenzoate (VI) by means of a mixture of 40 cc. of concd. acetic acid, 6 cc. of concd. hydrochloric acid and 4 cc. of water (stirred at room temperature for two hours) gave 0.21 g. of nearly pure enol benzoate (II) which was purified further and identified.

**2,3-Dihydroxy-1,4-dimesitylbutanedione-1,4** (1,2-dimesitylglycol) (III) was converted in 65% yield into the enol (I) upon treatment with 5% sodium hydroxide in methanol at 60–70° for five minutes.

**2-Hydroxy-1,4-dimesitylbutanedione-1,4.**—Attempts to prepare the benzoate by the use of benzoyl chloride gave only the product of dehydration, namely, dimesitylolethylene (VIII).

**1,4-Dimesityl-1,2,4-butanetrione silver enolate** was made by dissolving 3.5 g. of the sodium salt in 400 cc. of hot water, and cooling the filtered solution below 20°. Upon addition of 100 cc. of 2% silver nitrate the silver salt separated as a curdy, brilliant yellow precipitate which was filtered quickly, washed thoroughly on the filter with water and dried in a vacuum desiccator; yield, 4.2 g. It turned dark on long standing, and the fresh precipitate was unstable and darkened rapidly in the presence of solutions containing an excess of silver nitrate.

**1,4-Dimesitylbutane-1,2,4-trione 2-Enol Acetate<sup>6</sup> (IX).**—(a) A suspension of 3 g. of the sodium enolate in 50 cc. of dry isopropyl ether and 2 g. of acetyl chloride was refluxed for four hours. The filtered solution was then evaporated and the residue crystallized from ethanol (yield, 2.0 g. or 72%); m. p. 144°. From the filtrate 0.4 g. of enol was recovered. (b) The action of acetyl chloride on the silver enolate in absolute ethanol, begun at 0° and continued over one hour as the temperature rose to that of the room, gave a 35% yield of this same enol acetate.

**Acid hydrolysis** with a hydrochloric-acetic acid and water mixture (refluxing for thirty minutes) regenerated the enol (I).

Direct sunlight on an alcohol solution was without action.

**2-Acetoxy-1,4-dimesitylbutanedione** was found to be stable when heated at 140° under 40 mm. pressure, and could subsequently be distilled at this temperature under 2 mm. pressure in the vacuum oven, coming over as a yellow viscous oil which could be crystallized from ethanol.

**2,3-Diacetoxy-1,4-dimesitylbutanedione-1,4** (1,2-Dimesitylglycol Diacetate) (X).—A solution of 0.4 g. of dimesitylglycol in 20 cc. of acetic anhydride at 0° was treated with 2 drops of concd. sulfuric acid; the mixture was warmed to 70°, cooled and poured into ice water. After hydrolysis was complete, the product crystallized; 0.37 g. (63%); m. p. 178–180°. Repeated crystallizations from ethanol raised the melting point to 181°. It was identified by mixture melting point with an authentic sample.<sup>6</sup>

**Alkaline hydrolysis** with an excess of sodium methoxide (at room temperature for two hours) gave the enol (I). **Acid hydrolysis** by a mixture of concd. acetic and hydrochloric acids and water in the ratio by volume of 20:5:3, gave the enol acetate (IX).

A sample of the diacetate was subjected to the action of refluxing benzoyl chloride for six hours, and was recovered quantitatively unchanged.

### Summary

Benzoylation and acylation of 1,4-dimesitylbutane-1,2,4-trione enolate resulted chiefly in oxygen-acylation; the 2-enol acylates were the only products isolated. The structures were shown through synthesis by partial hydrolysis of the 1,4-dimesitylglycol diacylates, and by reduction through di-enols to 2-benzoyloxy- and 2-acetoxy-1,4-dimesitylbutanedione-1,4.

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(6) Gray and Fuson, *J. Org. Chem.*, **56**, 741 (1934).