The dinitrobenzoate was purified by crystallization from alcohol and obtained as small leaflets, m. p. 101–103°; yield about 0.1 g. *Anal.* Calcd. for $C_{26}H_{42}O_6N_2$: C, 65.24; H, 8.85. Calcd. for $C_{26}H_{40}O_6N_2$: C, 65.52; H, 8.46. Calcd. for $C_{25}H_{40}O_6N_2$: C, 64.63; H, 8.68. Found: C, 64.74, 64.55; H, 8.77, 8.91.

Summary

1. The thermal decomposition of α-tocopherol, leading to the formation of durohydroquinone and an unsaturated, aliphatic hydrocarbon, has been described.

2. A study of the degradation products obtained by oxidation with chromic acid has been reported.

These degradation products, isolated as such or in form of derivatives, are: acetone, diacetyl, dimethylmaleic acid, an acid $C_{16}H_{32}O_2$, a lactone $C_{21}H_{40}O_2$, a ketone $C_{18}H_{36}O$.

3. A structural formula is proposed for α-tocopherol derived from these degradation experiments.

α-Tocopherol is regarded as a substituted 6-hydroxychromane with a long aliphatic side chain attached to the pyran ring.

RAHWAY, NEW JERSEY RECEIVED FEBRUARY 1, 1938

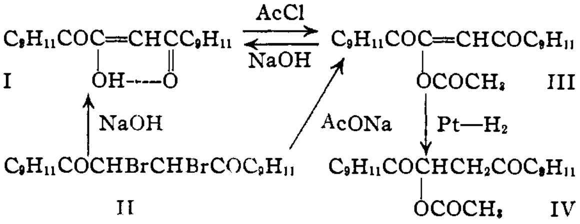
[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY OF THE UNIVERSITY OF VIRGINIA]

1,4-Dimesityl-1,2,4-butanetrione Enol and its Reduction Products

BY ROBERT E. LUTZ AND JOHN L. WOOD

In the light of recent work on the tautomerism of the 1,2,4-triketones and their reactions as open chain enols or as hydroxyfuranones, it seemed of interest to extend the studies on dimesitylbutanetrione enol, particularly because one would expect a marked influence of the mesityl groups not only on the reactivity of the systems involved but also on the tendency or ability to undergo cyclization.

Dimesitylbutanetrione enol, I, may be prepared either by the action of alcoholic alkali on di-(trimethylbenzoyl)-dibromoethane[1] (II) or by rearrangement of di-(trimethylbenzoyl)-ethylene oxide.[2] The ketonic form of this compound is at present unknown.[3] The enol reacts rapidly with bromine, diazomethane and ferric chloride, and is a relatively strong acid as shown by the fact that the sodium salt is precipitated when a petroleum ether solution is shaken with aqueous sodium carbonate. In contrast with the diphenyl analog it is not etherified with alcohol and acids, and there is at present no evidence to indicate that it can undergo cyclization to a hydroxyfuranone type. It does not undergo the quinoxaline reaction but it reacts readily with ketone reagents and gives a monoxime, a semicarbazone, and a 2,4-dinitrophenylhydrazone. The enol is converted by acetyl chloride and pyridine into an enol acetate in contrast with the diphenyl analog which gives the acetoxyfuranone under these conditions. The structure of the enol acetate is evident from analysis and acetyl determination, synthesis by the action of sodium acetate on di-(trimethylbenzoyl)-dibromoethane, II,[1a,3] and catalytic reduction to the acetate of di-(trimethylbenzoyl)-hydroxyethane, IV.



$$\begin{tikzcd}[column sep=small] \underset{\text{I}}{C_9H_{11}C(OH)\!=\!CHC(\!=\!O)C_9H_{11}} \arrow[r, shift left, "AcCl"] & C_9H_{11}C(OCOCH_3)\!=\!CHCOC_9H_{11}\ \text{III} \arrow[l, shift left, "NaOH"] \arrow[d, "Pt-H_2"] \\ \underset{\text{II}}{C_9H_{11}COCHBrCHBrCOC_9H_{11}} \arrow[u, "NaOH"] \arrow[ur, "AcONa"'] & C_9H_{11}COCH(OCOCH_3)CH_2COC_9H_{11}\ \text{IV} \end{tikzcd}$$

We have for convenience written the structure of the enol as I since reaction occurs largely in this sense upon acylation or on methylation with diazomethane. The latter reaction gives chiefly the yellow *trans*-di-(trimethylbenzoyl)-methoxyethylene, from which the colorless *cis* isomer has been made.[1b] However, on repetition of the experiments with diazomethane, two new yellow methyl ethers have been isolated in small amounts. These are evidently a stereoisomeric pair since the higher melting of the two (the labile and probably *cis* form) can be converted practically quantitatively into the lower melting, stable (and presumably *trans*) form by heating with alcoholic potassium hydroxide, exposing to sunlight in alcohol solution, or distilling *in vacuo*. The two new ethers are structurally isomeric with the two previously known ethers, and must be derivatives of the tautomeric enol form V. This was proved by

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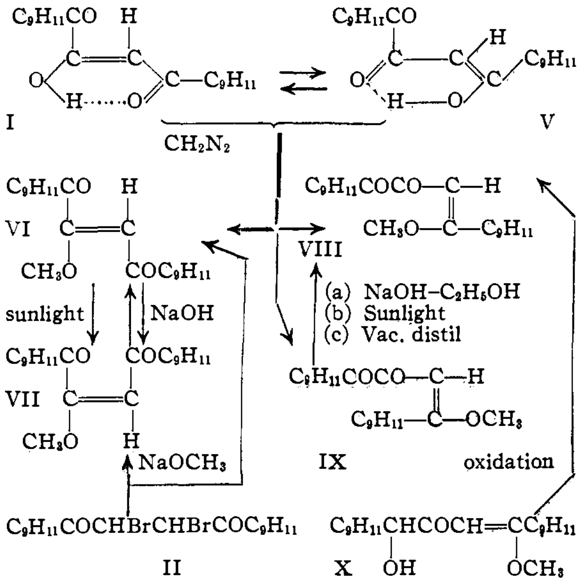
(1) Lutz, THIS JOURNAL, (a) **48**, 2905 (1926); (b) **56**, 1590 (1934).

(2) Lutz and Wood, *ibid.*, **60**, 229 (1938).

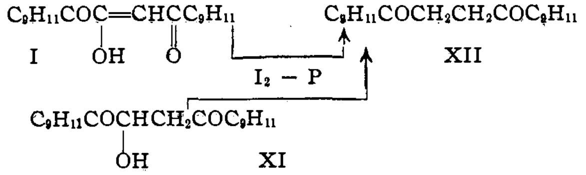
(3) The supposed keto form previously reported,[1a] prepared by the action of sodium acetate on di-(trimethylbenzoyl)-dibromoethane, is in reality the enol acetate III (see experimental part).

establishing the 4-position of the methoxyl groups through synthesis of the low melting isomer by oxidation of dimesityl-4-hydroxy-1,3-butanedione enol methyl ether, X, the structure of the latter being established by ozonization to trimethylbenzoic methyl ester. These relationships and the probable configurations are shown in the diagram.

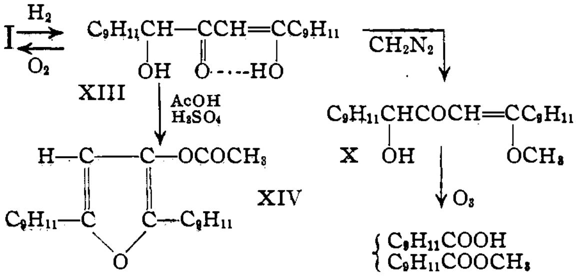


The stereoisomeric relationships are of interest and may be of some significance. Methylation would be expected to give only *trans* products since the arrangement of groups about the double bond in the parent enol is presumably fixed by the chelate ring involved. Methylation at the 4-oxygen (which occurs only to a limited extent) apparently produces both *cis* and *trans* products.

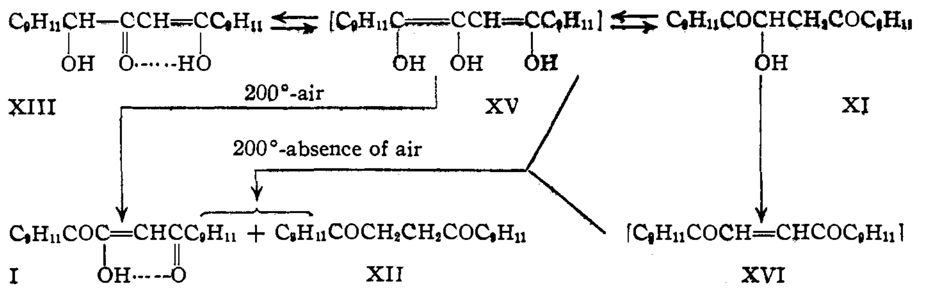
Reduction of dimesitylbutanetrione enol with the iodine–phosphorus–acetic acid reagent gives as the sole product di-(trimethylbenzoyl)-ethane, XII. Possibly the elimination of the hydroxyl occurs directly or from an intermediate such as XV or di-(trimethylbenzoyl)-hydroxyethane, XI, which is itself reduced to di-(trimethylbenzoyl)-ethane under these conditions.



In marked contrast with the above result, reductions of the enol with metal combinations such as zinc–ethanol–ammonium chloride, and with catalytic hydrogen, using Raney nickel, platinum, or palladium on barium sulfate, give high yields of a dihydro compound together with relatively small amounts of di-(trimethylbenzoyl)-ethane, XII. The new reduction product evidently has the structure XIII. Acetic anhydride and sulfuric acid convert it into acetoxydimesitylfuran, XIV. It behaves like a β-diketone enol and gives a deep red color with ferric chloride. It is acidic and forms a difficultly soluble sodium salt when a petroleum ether solution of the compound is shaken with aqueous sodium hydroxide, but it is less acidic than dimesitylbutanetrione enol since it does not react with sodium carbonate solution. It reacts with diazomethane readily and practically exclusively in the phase indicated in formula XIII, giving the enol ether X, the location of the methoxyl group being proved by ozonization to trimethylbenzoic methyl ester.



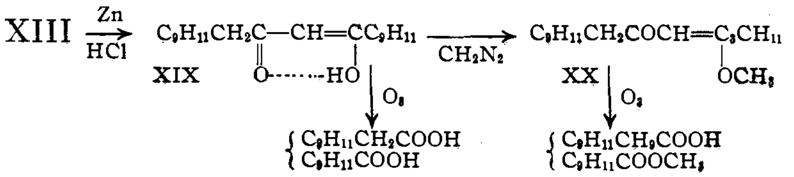
Oxidation of the dihydro compound XIII by air or oxygen takes place readily in alkaline solution or at elevated temperature, with regeneration of dimesitylbutanetrione enol, I. Disproportionation occurs at 200° in an inert atmosphere, giving di-(trimethylbenzoyl)-ethane, XII, and dimesitylbutanetrione enol, I. The mechanism of these reactions probably involves an equilibrium between XIII, di-(trimethylbenzoyl)-hydroxyethane, XI, and the hypothetical diene-triol XV, as suggested in the preceding paper.[2] The diene-triol XV, like ascorbic acid, should react readily with oxygen to give the triketone enol I. In the absence of air the compound itself in some form must act as the oxidizing agent and it seems likely that the hydroxy-1,4-diketone XI, assumed to be in equilibrium, is dihydrated to the unsaturated 1,4-diketone XVI which then could act as the acceptor for hydrogen and would be reduced in the process to di-(trimethylbenzoyl)-ethane, XII. The oxidizing action of di-(trimethylbenzoyl)-ethylene, XVI, on XIII was demonstrated in separate experiment, but the result was not completely satisfactory because



the yield of di-(trimethylbenzoyl)-ethane, XII, was not as high as could be desired and because considerable amounts of this latter product might have come from the disproportionation of XIII. By using di-(bromotrimethylbenzoyl)-ethylene, XVII,[4] as the oxidizing agent, however, good yields of the enol I and of di-(bromotrimethylbenzoyl)-ethane, XVIII, were obtained and no di-(trimethylbenzoyl)-ethane, XII, thus proving the point beyond question.

$$\text{XIII} + \underset{\text{XVII}}{BrC_9H_{10}COCH{=}CHCOC_9H_{10}Br} \longrightarrow \text{I} + \underset{\text{XVIII}}{BrC_9H_{10}COCH_2CH_2COC_9H_{10}Br}$$

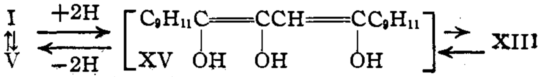
The enol methyl ether X, like the enol XIII, is oxidized easily, in this case to the enol ether VIII, presumably the *trans* form. Since the linkages responsible for the configurations are not involved in the oxidation, it is reasonable to suppose that the ether X corresponds in configuration and also is *trans*, and that the methylation of the enol XIII has proceeded in the expected stereochemical sense.



Further reduction of the dihydro compound XIII with zinc and hydrochloric acid or by means of the iodine–phosphorus reagent brings about elimination of the alcoholic hydroxyl group with formation of the β-diketone enol, dimesityl-1,3-butanedione enol, XIX. The new enol is acidic, gives a typical color reaction with ferric chloride, and gives a monoxime (with some difficulty). Ozonization produces mesitylacetic and trimethylbenzoic acids, showing that one terminal carbon of the chain is stripped of oxygen. Methylation with diazomethane gives a mixture consisting largely of the enol ether XX the structure of which was shown by ozonization to mesitylacetic acid and trimethylbenzoic methyl ester. Thus, like the dihydro compound XIII, and in contrast with dimesitylbutanetrione enol, I, the tetrahydro compound reacts largely in the sense of XIX, i. e., the form involving enolization at the carbonyl next to the mesityl group.

The different ways in which the three enols I, XIII, and XIX react on methylation with diazomethane is in accord with expectation. In the latter two cases (XIII and XIX) the β-diketone system is flanked by mesityl and trimethylbenzoyl, the latter of course having the greater influence and promoting reaction at the adjacent position; on the other hand, in I, the β-diketone system is flanked by mesityl and trimethylbenzoyl, the latter having the dominant influence, and the combined effect resulting in increased acidity.

The mechanism of reduction of dimesitylbutanetrione enol to the dihydro compound XIII is of interest because typical conjugated systems ending in carbonyl oxygens are involved. Undoubtedly, to a certain extent at least, hydrogen adds 1,4 or 1,6 to carbonyl oxygens of V or I with formation in either case of the intermediate dienetriol XV which then undergoes rearrangement to XIII.[5]



$$\begin{matrix}\text{I} \\ \updownarrows \\ \text{V}\end{matrix} \underset{-2H}{\overset{+2H}{\rightleftarrows}} \left[\underset{\text{XV}}{} C_9H_{11}\underset{OH}{C}{=}\underset{OH}{C}CH{=}\underset{OH}{C}C_9H_{11}\right] \rightleftarrows \text{XIII}$$

Evidence for this mechanism of reduction was found in the observation that catalytic hydrogenation produced a solution which very evi-

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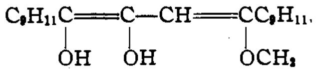
[4] Lutz, Johnson and Wood, THIS JOURNAL, **60**, 716 (1938).

[5] *Cf.* Lutz, THIS JOURNAL, **51**, 3008 (1929); Lutz and Palmer, *ibid.*, **57**, 1953, 1957 (1935); Kohler and Thompson, *ibid.*, **59**, 887 (1937).

dently contained large amounts of the intermediate diene-triol since like ascorbic acid and related compounds it absorbed oxygen of the air readily, losing two ene-diol or diene-diol hydrogens (1,4 or 1,6) and regenerating the yellow triketone enol I which was recovered. In the absence of air the intermediate changed slowly to the end-product XIII which is relatively stable and could then be isolated. The change was followed semi-quantitatively by titration under nitrogen with iodine for the amount of diene-triol present, 50% being found in a typical experiment 30 minutes after initiation of reduction.

In preliminary catalytic hydrogenations of the two new stereoisomeric enol ethers VIII and IX, one molecule of hydrogen was absorbed in each case giving colorless solutions which readily absorbed oxygen from the air, regenerating the two yellow triketone enol ethers which were recovered in typical experiments. Iodine titrations made thirty minutes after initiation of reduction indicated the presence of at least 70–80% of intermediate ene-diols of the type



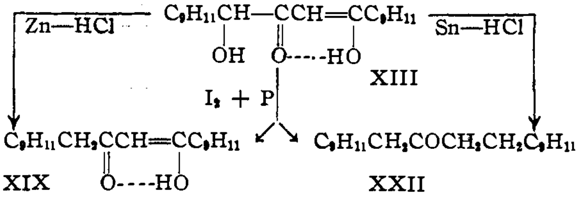
XXI

$$C_9H_{11}C(OH){=}C(OH){-}CH{=}C(OCH_3)C_9H_{11}$$

These must exist in two stable stereoisomeric forms since the solutions on oxidation regenerate, respectively, the two stereoisomeric ethers VIII and IX. Investigations in this field are being continued.

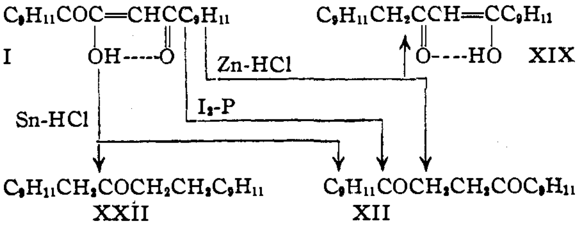
In this connection it is perhaps worth noting that the reduction of dimesitylbutanetrione enol, I, under many different conditions leads to dimesityl-4-hydroxy-1,2-butanedione enol and ultimately to dimesityl-1,3-butanedione enol, instead of giving the saturated 1,4-diketone XII and the corresponding diaroylhydroxyethane, XI, as happens in the reduction of diphenyl-1,2,4-butanetrione enol. The carbonyl next to a mesityl group has undergone preferential reduction as happens in other analogous cases, notably mesitylphenyl diketone, $C_9H_{11}COCOC_6H_5$,[6] and mesitylbenzyl diketone, $C_9H_{11}COCOCH_2C_6H_5$.[7]

Reduction under certain conditions of dimesitylbutanetrione enol, I, and the dihydro compound XIII leads to the formation of dimesitylbutanone-2, XXII, which is described in the following paper.[8] The reductions of the dihydro compound which are of particular interest in this connection are summarized in the following diagram.



Zinc and hydrochloric acid produced the β-diketone enol XIX exclusively, tin and hydrochloric acid gave chiefly the monoketone XXII, and the iodine–phosphorus–acetic acid reagent gave a mixture of XIX and XXII. Di-(trimethylbenzoyl)-ethane, XII, was not obtained in these reductions of XIII as it was in the reductions of the parent triketone enol I. The β-diketone enol XIX and the monoketone XXII are both stable and are not acted on further by prolonged contact with these reducing agents. They are therefore independent end-products. The formation of the β-diketone enol XIX obviously involves a simple reductive elimination of the alcoholic α-hydroxyl group directly or by a 1,4-reduction. The formation of the monoketone, however, since it cannot involve the β-diketone enol as an intermediate step, must take place through reduction at the end carbonyl (or enol) oxygen before or simultaneously with elimination of the alcoholic hydroxyl.

Dimesitylbutanetrione enol, I, with zinc or tin and hydrochloric acid also gives, respectively, the β-diketone enol XIX and the monoketone XXII, obviously in both cases through primary formation of the hydroxy-β-diketone enol XIII which itself gives these products under the same conditions. However, in the reductions of I considerable amounts of di-(trimethylbenzoyl)-ethane, XII, are produced consistently in addition, and in the iodine-phosphorus reduction the latter, XII, is the dominant product.



The formation of the saturated 1,4-diketone in these reductions cannot involve the hydroxydiketone enol XIII because the latter should not

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[6] Weinstock and Fuson, THIS JOURNAL, 58, 1233 (1936).

[7] Barnes, *ibid.*, 57, 937 (1935).

[8] Lutz and Wood, *ibid.*, 60, 713 (1938).

be, and is not, reducible to di-(trimethylbenzoyl)-ethane, XII, under these conditions, and must take place through direct elimination of the 2-hydroxyl from I, or through some other and less obvious mechanism.

Experimental Part

The Preparation of 1,4-Dimesityl-1,2,4-butanetrione Enol, I.—A solution of di-(trimethylbenzoyl)-ethylene (25 g.) in 125 cc. of hot concd. acetic acid was cooled quickly with stirring to produce fine crystals. A solution of 13 g. of bromine in 25 cc. of concd. acetic acid was then added slowly with stirring and cooling; the yellow crystals dissolved and a white crystalline precipitate appeared which was filtered by suction and washed with cold solvent. The thoroughly dried dibromide was suspended in 500 cc. of 80% methanol containing 18 g. of sodium hydroxide (a large excess). The mixture was boiled until complete solution resulted, and then for ten minutes longer. The sodium salt of the enol usually precipitated during this procedure. The mixture was then acidified with concd. hydrochloric acid, decanted from resinous material, and allowed to cool slowly. The enol separated almost pure as yellow crystals in yields of 60–65%.

The preparation from di-(trimethylbenzoyl)-ethylene oxide has been described in the preceding paper.[3]

Anal.[9] Calcd. for $C_{22}H_{24}O_3$: C, 78.5; H, 7.2. Found: C, 78.1; H, 7.0.

1,4-Dimesityl-2-acetoxy-2-butenedione-1,4 (Di-(trimethylbenzoyl)-acetoxyethylene), III.—The supposed 1,-4-dimesityl-1,2,4-butanetrione, reported in a previous paper,[1a] and prepared by the action of alcoholic sodium acetate on di-(trimethylbenzoyl)-dibromoethane, II, is in reality the acetate of the above described enol. The analyses reported (namely, C, 76.2, 76.4; H, 7.2, 7.1) are in good agreement with the values calculated for the acetate (calcd. for $C_{24}H_{26}O_4$: C, 76.2; H, 6.9). The compound does not react with the ketone reagents, hydroxylamine or semicarbazide, a fact which would appear to exclude the triketone formulation. Acetyl determination shows one acetyl.

This acetate has now been prepared directly from the enol I by allowing a mixture of 0.3 g., 3 cc. of pyridine, and 1 cc. of acetyl chloride to stand for eighteen hours. The mixture was decomposed in ice and hydrochloric acid and the product crystallized from ligroin: m. p. 144.5–145° (corr.); yield 0.27 g. It was shown to be identical with the product obtained by the action of sodium acetate on di-(trimethylbenzoyl)-dibromoethane by mixed melting points.

Anal. Calcd. for $C_{24}H_{26}O_4$: $COCH_3$, 11.4. Found: $COCH_3$, 10.9.

Catalytic reduction of 2.5 g. of the above enol acetate in 13 cc. of ethanol with 0.03 g. of platinum oxide showed absorption of approximately one molecule of hydrogen. Concentration of the solvent gave an oil from which small amounts of the enol acetate were recovered, formed presumably by air oxidation of some intermediate diene-diol. The oil finally crystallized, giving 0.29 g. of nearly pure di-(trimethylbenzoyl)-hydroxyethane.

In another experiment, a sample of the oil remaining was allowed to stand for two years. When treated with ligroin, di-(trimethylbenzoyl)-ethylene was isolated and identified, formed presumably by slow loss of acetic acid from the acetate.

Reactions of 1,4-Dimesityl-1,2,4-butanetrione Enol.—The **semicarbazone** was prepared in the usual way and crystallized from ethanol: m. p. 204° (corr.).

Anal. Calcd. for $C_{23}H_{27}O_3N_3$: N, 10.7. Found: N, 10.7.

The **oxime** was prepared by the action of hydroxylamine hydrochloride in pyridine, heating for two and one-half hours. It crystallized from 60% ethanol and melted at 170.5–171° (corr.).

Anal. Calcd. for $C_{22}H_{24}O_3N$: N, 4.0. Found: N, 3.7.

The **2,4-dinitrophenylhydrazone** was prepared by the action of 2,4-dinitrophenylhydrazine in ethanol containing a little acetic acid. It was yellow and crystallized from chloroform–methanol mixtures or from butanone; m. p. 234–235° (corr.).

Anal. Calcd. for $C_{28}H_{28}O_6N_4$: N, 10.9. Found: N, 11.0.

The **quinoxaline reaction** failed, even after four days of heating in ethanol with *o*-phenylenediamine. **Methanolic hydrogen chloride** was without effect on the enol, a sample being recovered quantitatively after standing for nine days in solution in this reagent. Dry hydrogen chloride was passed into a boiling alcohol solution of the enol without effect. **Acetyl chloride** with a trace of sulfuric acid was without effect on the enol. Attempts at **oxidation** with nitric acid gave a small amount of a colorless non-enolic compound; crystallized from benzene; m. p. 177–180°. It has not yet been investigated. The enol was recovered after attempted **hydrolysis** by refluxing for five days in a mixture of 10 cc. of concd. acetic acid, 15 cc. of concd. hydrochloric acid and 5 cc. of toluene.

Reduction of the enol with zinc dust and concd. acetic acid at 30, at 80, and at 100°, gave products which largely consisted of a zinc derivative which on acidification with hydrochloric acid gave 1,4-dimesityl-4-hydroxy-1,3-butanedione enol. From the reaction at 100° a 25% yield of di-(trimethylbenzoyl)-ethane was isolated also, separated from the enol by shaking out the latter from a ligroin solution by means of sodium hydroxide.

Reduction with Zinc–Ethanol–Ammonium Chloride.—A mixture of 27 g. of the enol, 4.5 g. of ammonium chloride, an excess of zinc dust, and 250 cc. of 80% ethanol was stirred for one hour, the temperature being maintained at 40–50°. The solution was filtered and acidified with hydrochloric acid. The product, the dihydro enol XIII, was then extracted with ether and obtained nearly pure on crystallization from ethanol; yield 88%.

Reduction with zinc and hydrochloric acid was carried out as follows: a stream of hydrogen chloride gas was bubbled for five hours through a refluxing mixture of 32 cc. of 78% ethanol, 3 g. of the enol and 4 g. of 30-mesh granulated zinc. The solution was filtered and poured into water and the precipitated material allowed to coagulate and settle out. The product was then taken up in ligroin and shaken with aqueous sodium hydroxide, the sodium enolate of 1,4-dimesityl-1,3-butanedione precipitating. The enol, liberated therefrom on acidification, weighed 0.7

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(9) The analysis previously reported is erroneous.[1a]

g. and melted at 100–101°. From the ligroin solution on evaporation 1.25 g. of di-(trimethylbenzoyl)-ethane was isolated and identified.

Reduction with tin and hydrochloric acid, carried out by subjecting the enol for ten hours to the action of a boiling mixture of equal parts of concd. acetic and hydrochloric acids and 20 mesh granular tin, gave crude mixtures from which yields of 20–40% of nearly pure dimesitylbutanone-2 and 5% of nearly pure di-(trimethylbenzoyl)-ethane were isolated. Considerable amounts of oils were recovered which could not be crystallized.

Reduction with Iodine and Phosphorus.—A mixture of 1 g. of enol, 25 cc. of 95% acetic acid, 0.5 g. each of red phosphorus, and iodine was refluxed for two hours, filtered, poured into dilute sodium bisulfite solution, and the product extracted into ether. The oil obtained on evaporation of the solvent crystallized from ethanol, giving 0.25 g. of nearly pure di-(trimethylbenzoyl)-ethane.

Catalytic Reduction.—Hydrogenations using palladium on barium sulfate, platinum, or Raney nickel, in 95% ethanol, proceeded rapidly with the absorption of one molecule of hydrogen, and gave 1,4-dimesityl-4-hydroxy-1,3-butanedione enol in yields as high as 80–85%. If the solutions were not allowed to stand a sufficiently long time before removing from the atmosphere of hydrogen, some dimesityl-1,2,4-butanetrione enol was formed by oxidation of the intermediate diene-triol. Occasionally traces of di-(trimethylbenzoyl)-ethane were isolated, and there always remained some oily by-product which failed to crystallize.

Several reductions were carried out using ethanol as solvent with platinum catalyst, and titrating the resulting colorless solution with standard iodine solution under an atmosphere of hydrogen within thirty minutes after initiation of hydrogenation, 42–49% of two equivalents of iodine being used up. Very considerable amounts of the triketone enol I could then be isolated from the solution. Another experiment, in which the acidified solution was allowed to stand for two days before titrating, showed a negligible reaction with iodine and the dihydro compound XIII was isolated in good yield.

Methylation of 23 g. of the enol I with an excess of diazomethane in ether solution took place rapidly with vigorous evolution of nitrogen. The yellow product was crystallized repeatedly from ethanol, methanol, and ligroin, and gave as the main product the yellow *trans*-di-(trimethylbenzoyl)-methoxyethylene, VI, as square yellow plates melting at 113–114°. The residues were subjected to an extensive fractional crystallization from ethanol, and from ligroin, and yielded 2.7 g. of a yellow structural isomer melting at 145° (irregular hexagonal crystals), which proved to be 1,4-dimesityl-4-methoxy-3-butene-1,2-dione, IX, and was named isomer-A. Still another yellow and more soluble isomer was obtained in varying amounts, which crystallized as short rods melting at 127–128°, and which proved to be the stereoisomer, VIII, and was therefore called isomer-B. The latter was best prepared, however, by oxidation of the methyl ether of 1,4-dimesityl-4-hydroxyl-1,3-butanedione enol, X, as described below.

1,4-Dimesityl-4-methoxy-3-butene-1,2-dione-A (*Cis?*), **IX,** isolated as described above, was purified by repeated crystallization from alcohol and melted at 151–152° (corr.).

Anal. Calcd. for $C_{23}H_{26}O_3$: C, 78.8; H, 7.5; OCH_3, 8.9. Found: C, 78.7; H, 7.7; OCH_3, 9.0.

When exposed to sunlight in ethanol for six hours, this ether was transformed quantitatively into the lower melting isomer-B. When a solution in 1% methanolic potassium hydroxide was refluxed for five hours, the isomer-B was obtained in good yield. This conversion was effected also when the ether was distilled in the vacuum oven at 150°.

Reduction of 0.3 g. in ethanol with platinum catalyst showed rapid absorption of one molecule of hydrogen, giving a colorless solution. This was titrated under hydrogen within thirty minutes after initiation of hydrogenation with standard iodine solution and reacted with 71% of two equivalents. The solution when worked up gave starting material in good yield, which was identified by mixed melting point.

1,4-Dimesityl-4-methoxy-3-butene-1,2-dione-B (*trans?*), **VIII.**—The crude product from the methylation with diazomethane of 3 g. of 1,4-dimesityl-4-hydroxy-1,3-butanedione enol, XIII, was dissolved in methanolic potassium hydroxide and oxygen bubbled through the refluxing solution for forty-five minutes. The yellow solution was then acidified, and deposited 0.8 g. of nearly pure product melting at 127°. It was purified by repeated crystallization from alcohol; m. p. 127–128° (corr.).

Anal. Calcd. for $C_{23}H_{26}O_3$: C, 78.8; H, 7.5; OCH_3, 8.9. Found: C, 79.1; H, 7.4; OCH_3, 8.9.

The ether was recovered unchanged after long refluxing in 80% or pure methanol and potassium hydroxide, or sodium methylate solution. Apparently the ethers with the alkoxyl adjacent to the mesityl group are extraordinarily difficult to hydrolyze under these conditions. Di-(trimethylbenzoyl)-methoxyethylene is hydrolyzable, though not rapidly under these conditions, whereas dibenzoylmethoxyethylene is hydrolyzed rapidly.

Reduction of 1 g. with zinc–ammonium chloride–dilute methanol gave an oil from which 0.4 g. of di-(trimethylbenzoyl)-ethane was isolated. Reduction of 0.5 g. of the ether-B in ethanol with platinum catalyst showed a rapid absorption of one mol of hydrogen, the solution becoming colorless. Titration within thirty minutes of initiation of hydrogenation with standard iodine solution showed 78–80% of ene-diol to be present, and subsequently the isomer-B was recovered in good yield and identified.

1,4-Dimesityl-4-hydroxy-1,3-butanedione enol, XIII, was best prepared by either the zinc–alcohol–ammonium chloride or the catalytic reductions of the triketone enol, I, as described above. It was obtained after repeated crystallization from ethanol as fine colorless needles melting at 104.5–105.5° (corr.). It could be distilled without change in the vacuum oven.

Anal. Calcd. for $C_{22}H_{26}O_3$: C, 78.1; H, 7.75. Found: C, 78.2, 78.0; H, 7.95, 7.9.

When the samples of the above contained small amounts of di-(trimethylbenzoyl)-ethane, recrystallizations were not sufficient to effect purification. In that case the crude materials were dissolved in a 50–50 petroleum ether–ligroin mixture and shaken out with strong sodium bicarbonate solution which caused the precipitation of the yellow sodium salt of dimesityl-1,2,4-butanetrione enol (small amounts were usually formed by oxidation of the product or of intermediates in the reduction process). After filtering, the ether–ligroin mixture was again shaken out, this time with 5% sodium hydroxide solution, the colorless sodium salt of the dihydro enol XIII being precipitated. The enols were recovered from the salts by decomposing under ether with dilute hydrochloric acid, care being taken in the case of the dihydro compound to avoid undue exposure of the solutions to air. Evaporation of the ether–ligroin solution remaining after precipitation of the sodium enolates contained the di-(trimethylbenzoyl)-ethane which could subsequently be isolated and crystallized from ethanol or ligroin.

The dihydro enol XIII gives a deep red color with ferric chloride, decolorizes bromine in carbon tetrachloride instantly, and forms a sodium salt readily (but does not dissolve) in aqueous sodium hydroxide solution.

Conversion into 3-acetoxy-2,5-dimesitylfuran was effected by the action of acetic anhydride and a few drops of concd. sulfuric acid at room temperature on the above dihydro compound XIII. **Attempts to prepare a 2,4-dinitrophenylhydrazone** by the interaction of 0.3 g. of XIII and 0.3 g. of 2,4-dinitrophenylhydrazine in ethanol and a few drops of concd. acetic acid (refluxing two hours) gave, instead of the expected hydrazone, 0.22 g. of orange-red crystals melting at 115–116° (corr.). (*Anal.* N, 21.6%.) Attempts to make a *semicarbazone* and an *oxime* failed. *Acetyl chloride* reacted to give an intractable oil. *Chromic acid oxidation* did not give tractable products. *Concd. nitric acid* converted the compound into a colorless non-enolic product melting at 152–159° which was not further investigated. Attempts to bring about *rearrangement* by heating with acetic acid, with and without sodium acetate, failed, although in one experiment which could not be duplicated some di-(trimethylbenzoyl)-hydroxyethane was produced.

Oxidation.—A stream of dry air was passed over a sample of XIII at 200° for one and a half hours and the products then vacuum distilled onto a cold finger condenser. Crystallization of the distillate gave dimesityl-1,2,4-butanetrione enol melting at 110–111°.

Disproportionation.—A sample of XIII was heated at 200–210° under nitrogen for one hour and then vacuum distilled onto a cold finger condenser. The resulting mixture was crystallized from ligroin, giving di-(trimethylbenzoyl)-ethane. The filtrate was treated successively with sodium carbonate and sodium hydroxide solutions, giving in succession the sodium salts of dimesityl-1,2,4-butanetrione enol and unchanged XIII (identified by acidification and recovery of the free enols). Evaporation of the ligroin solution remaining gave more di-(trimethylbenzoyl)-ethane. Similar results were obtained when the dihydro compound XIII was treated with 78% methanol containing an excess of sodium hydroxide, the yield of XII being larger when air was present during the reaction. When boiling 10% sodium hydroxide was used, again disproportionation occurred, but no hydrolytic splitting.

Oxidation of 1,4-Dimesityl-4-hydroxy-1,3-butanedione Enol by Unsaturated 1,4-Diketones.—A mixture of 1.5 g. of XIII and 0.75 g. of di-(trimethylbenzoyl)-ethylene was heated at 200–210° under a stream of nitrogen for one hour and the products worked up as described above; 0.72 g. of di-(trimethylbenzoyl)-ethane was recovered, together with 1.14 g. of crude sodium salt of the triketone enol (I). Pyrolysis under similar conditions of a mixture of the triketone enol I and di-(trimethylbenzoyl)-ethylene and the saturated 1,4-diketone XII was without effect on these materials.

In a similar experiment, 0.2 g. of XIII and 0.28 g. of di-(bromotrimethylbenzoyl)-ethylene gave 0.15 g. of dimesitylbutanetrione enol and 0.2 g. of di-(bromotrimethylbenzoyl)-ethane, the rest of the material being accounted for largely as resinous by-products from which no di-(trimethylbenzoyl)-ethane was isolated.

Reduction with iodine and phosphorus under a variety of conditions gave varied and inconsistent results. In a typical experiment, 8 g. of XIII was treated with 100 cc. of 96% acetic acid, and 4 g. each of iodine and red phosphorus, the mixture being refluxed for one and a half hours. After filtering and diluting with water 4 g. of crude product was obtained. When taken up in ligroin and shaken with sodium hydroxide solution a sodium salt precipitated and gave on acidification dimesityl-1,3-butanedione enol. From the ligroin solution which remained dimesitylbutanone-2 was isolated and identified.

Reductions with tin and zinc and hydrochloric acid are described under the preparation of the respective products obtained, namely, dimesitylbutanone-2 and dimesityl-1,3-butanedione enol.

1,4-Dimesityl-1-hydroxy-4-methoxy-3-butenone-2, X.—The enol XIII, when treated with an excess of diazomethane in ether, gave an oil which finally solidified. It crystallized from ethanol and from ligroin as colorless rhombic prisms of m. p. 149–150° (corr.).

Anal. Calcd. for $C_{23}H_{28}O_2$: C, 78.4; H, 8.0; OCH_3, 8.8. Found: C, 78.4; H, 7.9; OCH_3, 8.4.

From the mother liquors evidence of a second compound was noted and a few crystals picked out by hand (m. p. 135°).

Oxidation was effected by passing a stream of air over the fused ether at 200° for fifteen minutes. On subsequent distillation in the vacuum oven a yellow oil was obtained from which a pure sample of *trans*-1,4-dimesityl-4-methoxy-3-butene-1,2-dione was isolated and identified by a mixed melting point with the preparation described below.

Attempted hydrolysis and acylation with acetic anhydride and pyridine gave non-crystalline products.

Ozonization of 2.9 g. of the ether X in 20 cc. of dry chloroform for four hours, with subsequent evaporation of the solvent, hydrolysis with sodium bicarbonate, and extraction with ether, gave a neutral fraction containing considerable unreacted material which was again ozonized for ten hours and worked up in the same way. The final neutral oil was distilled, the first fraction boiling at 62–72° at 3–5 mm. pressure. This was poured into fuming nitric acid and the mixture decomposed in ice water. The dinitro compound solidified (yield 0.33 g.) and on one crystallization from ethanol melted at 137.5–139° (identified as dinitrotrimethylbenzoic methyl ester by mixed melting point with an authentic sample prepared as described below). A small sample of trimethylbenzoic acid was isolated from the acid fractions and was identified.

Obviously the difficulty of ozonization, as contrasted with the ease with which di-(trimethylbenzoyl)-methoxyethylene is attacked and split by this reagent, is due to the steric effect of the mesityl group attached directly to the enol ether double bond.

3,5-Dinitro-2,4,6-trimethylbenzoic methyl ester was obtained by the action of diazomethane in ether on trimethylbenzoic acid followed by nitration with cold fuming nitric acid. It was crystallized from ethanol or ligroin and melted at 140.5–141° (corr.) (colorless).

Anal. Calcd. for $C_{11}H_{12}O_6N_2$: C, 49.3; H, 4.5. Found: C, 49.1; H, 4.5.

1,4-Dimesityl-1,3-butanedione enol, XIX.—Dry hydrogen chloride was passed through a well-stirred mixture of 5 g. of dimesityl-4-hydroxyl-1,3-butanedione enol, 54 cc. of 88% ethanol, and 3 g. of zinc dust at refluxing temperature for two hours. The solution was decanted, poured into water, and the resulting oil extracted into ligroin from which the enol was precipitated as the sodium salt by shaking with aqueous sodium hydroxide (yield 78%). The enol was obtained from the salt on acidification and was crystallized from ligroin; m. p. 103.5–104.5° (corr.).

Anal. Calcd. for $C_{22}H_{26}O_2$: C, 81.9; H, 8.1. Found: C, 81.7; H, 7.9.

The **oxime** was prepared by treating the enol with hydroxylamine hydrochloride in pyridine and refluxing for two and a half hours. It was crystallized from isopropyl ether; m. p. 125–125.5° (corr.).

Anal. Calcd. for $C_{22}H_{27}O_2N$: N, 4.0. Found: N, 4.1.

Attempts to prepare a semicarbazone and a 2,4-dinitrophenylhydrazone failed. Hydrolysis with boiling barium or sodium hydroxide solutions did not have any effect. Attempted reductions with iodine and phosphorus and with tin and hydrochloric acid under the usual conditions also were without effect, the compound being recovered nearly quantitatively unchanged in each case (checked in duplicate experiments).

Ozonization of 1.5 g. in 15 cc. of dry chloroform at 0° for four hours, with subsequent evaporation of the solvent, hydrolysis, and extraction with sodium bicarbonate and ether, gave a neutral extract which appeared to contain mesityl glyoxal, giving the characteristic red color with sirupy phosphoric acid[10] (this was not conclusively proved, however). The sodium bicarbonate extract on acidification gave 1.97 g. of solid which was esterified by means of methanolic hydrogen chloride (standing overnight). The product was then extracted with sodium carbonate to remove trimethylbenzoic acid (unaffected by this treatment) which was subsequently isolated in a yield of 0.18 g. (identified by mixed melting point with an authentic sample prepared from bromomesitylene through the action of carbon dioxide on the Grignard reagent). The ether solution gave an oily ester which was hydrolyzed by boiling with 12 cc. of 5% sodium hydroxide for half an hour. Acidification of this solution gave a crystalline acid which was recrystallized from water and melted at 163–164.5° (yield 0.16 g.). Further purification by crystallization from ligroin gave a m. p. of 165.5–166.5°.[11] The mesitylacetic acid was further identified by conversion into the amide (m. p. 210.5–211.5°) by the action of thionyl chloride followed by ammonium hydroxide (crystallized from dilute ethanol), and by conversion into dinitromesitylacetic acid by the action of fuming nitric acid (m. p. 238–241° (corr.),[12] and through subsequent esterification of this to the dinitro methyl ester melting at 140.5–141.5° (Meyer reported 140–141°[12]).

1,4-Dimesityl-4-methoxy-3-butanone-2, XX.—1,4-Dimesityl-1,3-butanedione enol XIX (6 g.) was treated with 1.5 g. of diazomethane in ether solution. From the white crystalline product 3.3 g. of nearly pure product was obtained on crystallization from isopropyl ether. It was recrystallized from chloroform–ligroin mixtures and melted at 148.5–149.5° (corr.).

Anal. Calcd. for $C_{23}H_{28}O_2$: C, 82.1; H, 8.4; OCH_3, 9.2. Found: C, 82.1; H, 8.4; OCH_3, 9.0.

From the lower melting residues of the above procedure, by a series of fractional crystallizations, we succeeded in isolating a small amount of a second substance as long colorless needles of m. p. 135–136.5° (corr.). This proved to be an isomer but we did not have sufficient material to prove its structure.

Anal. Calcd. for $C_{23}H_{28}O_2$: C, 82.1; H, 8.4; OCH_3, 9.1. Found: C, 82.0; H, 8.5; OCH_3, 8.8.

In addition to the above isomer, a trace of a third high melting compound (m. p. 175–176°) was isolated, but not in sufficient quantity for study.

Oxime.—A solution of 0.1 g. each of the ether XX and hydroxylamine hydrochloride in pyridine was heated for two hours and 0.08 g. of the oxime was obtained. It was crystallized from butanone and melted at 182–186°.

Anal. Calcd. for $C_{23}H_{29}O_2N$: N, 4.0; OCH_3, 8.8. Found: N, 3.7; OCH_3, 8.3.

Ozonization.—A stream of ozonized oxygen was passed for five hours through a dry chloroform solution (15 cc.) of 2.9 g. of the ether XX (of m. p. 148.5°), the solvent subsequently evaporated under reduced pressure and the residue hydrolyzed with sodium bicarbonate and extracted with ether. Since the reaction was evidently far from complete the oil obtained from the ether solution was taken up in chloroform (distilled partly to dry it) and again ozonized for twelve hours with subsequent treatment as before. Finally a third ozonization for five hours was carried out. The final neutral oil obtained (0.89 g.) was distilled, giving a fraction of 0.3 g. of b. p. 68–72° at 3–5 mm. pressure which showed a b. p. of 242–245° (corr.) at 754 mm. (as compared with a b. p. of 242–244° (corr.) reported for trimethylbenzoic methyl ester[13]). This material was further identified by conversion into the dinitro derivative which was identified by mixed melting point with an authentic sample.

From the sodium bicarbonate extract upon acidification and extraction with ether, a partly crystalline product was obtained and washed with ether–petroleum ether mixtures, reprecipitated from ammoniacal solution by acids, and repeatedly crystallized from ethanol and from ligroin. Characteristic needle crystals of trimethylphenylacetic acid were isolated (m. p. 166–167°) and identified by mixed melting point with the sample described above.

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[10] Gray and Fuson, This Journal, **56**, 739 (1934).

[11] *Cf.* Claus, *J. prakt. Chem.*, [2] **41**, 504 (1890).

[12] *Cf.* Meyer, *Ber.*, **29**, 1413 (1896).

[13] Feith and Davies, *ibid.*, **24**, 3546 (1891).

The above ozonization proceeded with considerable difficulty and again there appears to be marked steric hindrance due to the mesityl groups attached directly to the enol ether double bond.

Summary

The preparation and reactions of dimesitylbutanetrione enol are described, including the formation of ketone derivatives and the enol acetate. In the reaction with diazomethane a new stereoisomeric pair of methyl ethers is reported with discussion of the structures and stereochemistry involved.

Reductions of the enol under a variety of conditions are described.

The preparation and reactions of dimesityl-4-hydroxy-1,3-butanedione enol are discussed, including dehydration to acetoxydimesitylfuran, methylation with diazomethane, oxidation and disproportionation. The mechanism of the latter reaction is considered.

The proof of structure and reactions of dimesityl-1,3-butanedione enol are outlined, including methylation and ozonization of the enol and its ether.

The mechanisms of many of the reductions are discussed, particularly the proof that, in the case of the triketone enol and the two new enol ethers, addition of hydrogen occurred at the ends of conjugated systems ending in carbonyl groups.

Charlottesville, Va. Received January 18, 1938

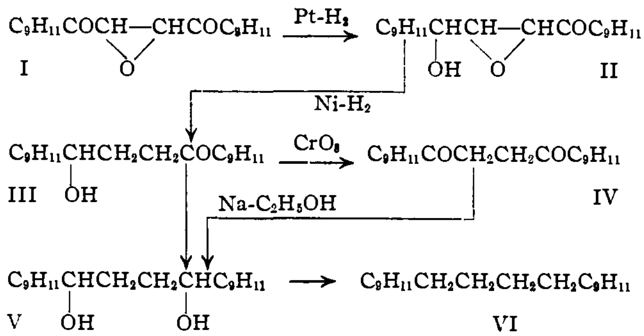
[Contribution from the Cobb Chemical Laboratory, University of Virginia]

The 1,4-Dimesitylbutanones

By Robert E. Lutz and John L. Wood

1,4-Dimesitylbutanones-1 and -2 were prepared in the course of the studies on the reduction of di-(trimethylbenzoyl)-ethylene oxide and dimesitylbutanetrione enol, which have been described in two preceding papers.[1] One of these, dimesitylbutanone-2, is of particular interest because it is obtained in several instances as a direct reduction product. The other, dimesitylbutanone-1, was made incidentally in order to complete the preparation of the four possible monoketo and monohydroxy derivatives. These compounds were all interrelated and degraded finally to dimesitylbutane in order to show beyond any question that the chain remained intact throughout all of the various transformations described.

Dimesitylbutanone-1, X, was prepared indirectly from dimesityl-4-hydroxybutanone-1, III, the latter compound being obtained from di-(trimethylbenzoyl)-ethylene oxide, I, in two steps as shown in the following diagram. The structure of the hydroxy ketone III was established by oxidation with chromic acid to di-(trimethylbenzoyl)-ethane, IV, and by reduction with sodium and alcohol to dimesityl-1,4-dihydroxybutane, V, which was obtained in another way by sodium and alcohol reduction of di-(trimethylbenzoyl)-ethane, IV. The glycol V in turn was reduced in steps by treatment first with the iodine–phosphorus reagent and then with sodium and ethanol, to dimesitylbutane, VI, which is known.[2]



The first attempts to prepare dimesitylbutanone-1 from the hydroxy ketone III through reductive elimination of the alcoholic hydroxyl group by heating with the iodine–phosphorus reagent, brought about instead the elimination of the elements of water to give an unsaturated ketone (VII). This product was obtained also by replacement of the hydroxyl of III with chlorine, followed by elimination of hydrogen chloride upon heating. An isomeric unsaturated ketone (IX) was obtained from the chloro ketone

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[1] Lutz and Wood, This Journal, **60**, (a) 229, (b) 705 (1938).

[2] Sorde, *Compt. rend.*, **195**, 247 (1932).