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

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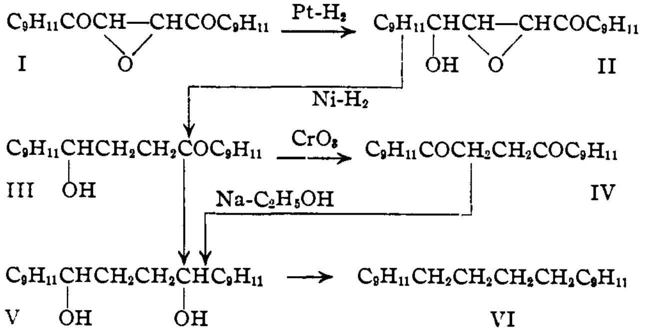
[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA]

# 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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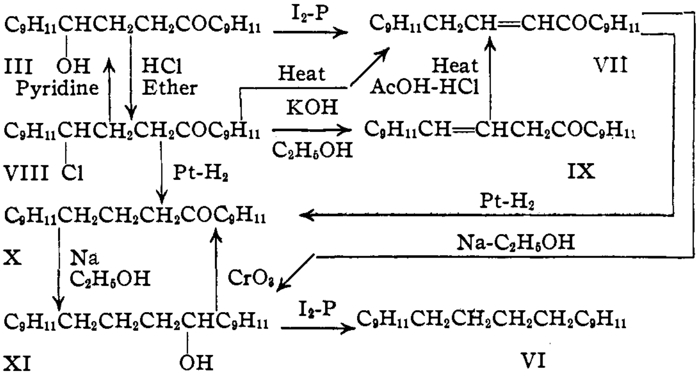
[1] Lutz and Wood, THIS JOURNAL, **60**, (a) 229, (b) 705 (1938).

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

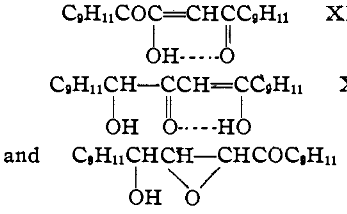
VIII when hydrogen chloride was eliminated by means of alcoholic potassium hydroxide. This isomer (IX) is the less stable of the two and is transformed into the first (VII) when heated in acetic acid in the presence of hydrogen chloride. In view of this rearrangement it is obvious that the unstable isomer is the $\beta,\gamma$-unsaturated ketone and the stable one the $\alpha,\beta$-, as formulated in the following diagram, and that in the elimination of water and hydrogen chloride, respectively, from III and VIII under comparable conditions, the unstable isomer IX is formed first and quickly rearranged into VII. Dimesitylbutanone-1, X, was then obtained by catalytic hydrogenation of either the chloro ketone VIII or the $\alpha,\beta$-unsaturated ketone VII.



The position of the carbonyl group in dimesitylbutanone-1 follows from the foregoing relationships which connect the ketone with di-(trimethylbenzoyl)-ethane, IV. The carbonyl group is subject to steric hindrance and is unreactive toward typical ketone reagents. Reduction of the ketone X and also the unsaturated ketone VII by means of sodium and ethanol gave the corresponding alcohol, dimesitylbutanol-1, XI, which was oxidized back to the ketone X by means of chromic acid. The alcohol was converted by means of the iodine–phosphorus reagent into dimesitylbutane, VI.

In connection with the above reactions two incidental facts are worth noting: first, the chloro ketone VIII loses hydrogen chloride to give the unsaturated compound IX when heated with methanolic potassium hydroxide whereas it is hydrolyzed to the hydroxy ketone III when heated with pyridine. And, second, the $\beta,\gamma$-unsaturated ketone IX did not undergo reduction in an experiment carried out under the same conditions as were employed in reducing the isomeric $\alpha,\beta$-unsaturated ketone VII, a result which might possibly be interpreted in terms of steric hindrance.

Dimesitylbutanone-2, XV, together with other products, was obtained in the reductions of the following



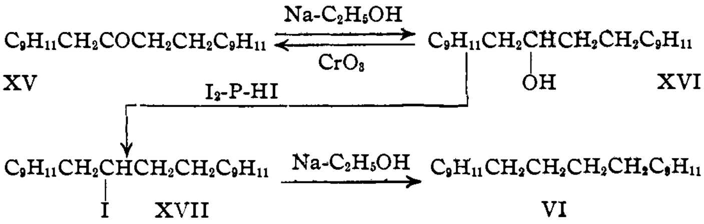
$C_9H_{11}CO\underset{OH}{C}{=}CH\underset{O}{\overset{\|}{C}}C_9H_{11}$ XII

$C_9H_{11}\underset{OH}{CH}—\underset{O}{\overset{\|}{C}}CH{=}\underset{HO}{C}C_9H_{11}$ XIII

and $C_9H_{11}\underset{OH}{CH}CH—CHCOC_9H_{11}$ (epoxide O bridging the two CH) XIV

The carbonyl group must be in the 2-position since this compound is isomeric with dimesitylbutanone-1. In contrast with the isomer X it gives a monoxime, a semicarbazone, and a 2,4-dinitrophenylhydrazone. The carbonyl group is therefore unhindered and cannot have its carbonyl in a terminal position, thus confirming independently the structure XV.

Sodium and alcohol reduction of dimesitylbutanone-2 gave the corresponding alcohol, XVI. The latter reacted with phenyl isocyanate to give a typical urethan, and could be oxidized back to the ketone with chromic acid; the action of iodine, phosphorus and hydriodic acid gave the iodide XVII which was then reduced with sodium and alcohol to dimesitylbutane, VI.



## Experimental

**1,4-Dimesityl-1,4-dihydroxybutane, V.**—A sample of 1,4-dimesityl-4-hydroxybutanone-1 (0.28 g.) was reduced in 30 cc. of absolute ethanol under nitrogen with 5 g. of sodium. On diluting with water, 0.07 g. of the glycol melting at 180–182° was obtained. When 2 g. of di-(trimethylbenzoyl)-ethane was reduced under similar conditions a mixture, presumably of the two possible stereoisomeric glycols, was obtained, from which on crystallization from methanol 0.62 g. of the same compound melting at 177–180° was isolated. After repeated crystallization from ethanol it melted at 184.5–185.5° (corr.).

*Anal.* Calcd. for $C_{22}H_{30}O_2$: C, 80.9; H, 9.3. Found: C, 80.6; H, 9.2.

**1,4-Dimesitylbutane, VI.**—(a) A mixture of 0.25 g. of the above glycol, 0.05 g. each of iodine and red phosphorus, 8 cc. of concd. acetic acid, 3 drops of water and 3 drops of hydriodic acid (sp. gr. 1.7) was heated for one and one-half hours and decomposed in dilute sodium bisulfite solution. The organic material was extracted into ether, the acids shaken out by 5% sodium hydroxide, and the ether evaporated. The residue was crystallized from ethanol; yield 0.11 g. melting at 84–94°. The product contained halogen and was then subjected to reduction in 15 cc. of absolute ethanol with 1.5 g. of sodium (under nitrogen). On diluting with water fine crystals of dimesitylbutane formed and after three crystallizations from ethanol melted at 123–124° (the m. p. 124° was reported by Sorde[2]).

(b) Three-tenths gram of 1,4-dimesitylbutanol-1, XI, was treated with 0.4 cc. of hydriodic acid (sp. gr. 1.7), 0.07 g. of red phosphorus and 1 cc. of concd. acetic acid, refluxing for eight hours. The product was precipitated by diluting with water, and crystallized as needles (0.17 g.) from ethanol; m. p. 125.5–126°.

(c) Reduction of 0.067 g. of 1,4-dimesityl-2-iodobutane XVII, in absolute ethanol with 1 g. of sodium under nitrogen gave on dilution with water 0.044 g. of colorless needles which on crystallization from benzene and alcohol melted at 123.5–124.5°.

All the above preparations were proved identical by mixed melting points (other compounds of similar melting points in this series showed large mixed m. p. depressions).

*Anal.* Calcd. for $C_{22}H_{30}$: C, 89.7; H, 10.3. Found: C, 89.5; H, 10.2.

**1,4-Dimesityl-4-chlorobutanone-1, VIII.**—A solution of 0.5 g. of 1,4-dimesityl-4-hydroxybutanone-1, III, in chloroform was treated with 0.35 g. of phosphorus pentachloride, the temperature held at 15°. When the evolution of hydrogen chloride ceased the mixture was hydrolyzed, the chloroform solution evaporated, and the resulting oil then crystallized from petroleum ether (yield nearly quantitative). Similar results (but poorer yields) were obtained when III was allowed to stand overnight in dry ethereal hydrogen chloride. Recrystallization from ligroin gave a product melting at 102.5–103° (corr.).

*Anal.* Calcd. for $C_{22}H_{27}OCl$: C, 77.1; H, 7.9. Found: C, 77.6, 76.8; H, 8.1, 7.5.

**Hydrolysis** to dimesityl-4-hydroxybutanone-1 was brought about by heating a sample of the chloro ketone VIII in pyridine for thirty minutes.

**Pyrolysis** of 1 g. at 130° for 15 minutes, then crystallization from ethanol, gave 0.8 g. of dimesityl-2-butenone-1, VII. In a similar experiment in which the sample was heated for thirty minutes in boiling concd. acetic acid, VII was obtained in smaller yield.

**1,4-Dimesityl-3-butenone-1, IX.**—One gram of the chloro ketone VII was heated for one hour in an excess of methanolic potassium hydroxide, giving 0.45 g. of crude product which, after repeated recrystallization from ethanol, melted at 114° (corr.).

*Anal.* Calcd. for $C_{22}H_{26}O$: C, 86.2; H, 8.6. Found: C, 86.0; H, 8.4.

**Rearrangement** of 0.12 g. was effected by passing dry hydrogen chloride through a refluxing solution in 3 cc. of concd. acetic acid for one and one-half hours; the yield of VII was 0.7 g. Hydrogenation, using platinum catalyst and ethanol as solvent, was without effect on IX.

**1,4-Dimesityl-2-butenone-1, VII.**—A mixture of 0.5 g. of iodine, 2 g. of red phosphorus, 37 cc. of 95% acetic acid, and 4 g. of 1,4-dimesityl-4-hydroxybutanone-1, III, was refluxed for four hours and, on hydrolysis with an excess of sodium bisulfite solution, gave 2.8 g. of product melting at 108°. On crystallization from ethanol it melted at 116.5–117.5° (corr.).

*Anal.* Calcd. for $C_{22}H_{26}O$: C, 86.2; H, 8.6. Found: C, 86.3; H, 8.5.

When heated with methanolic potassium hydroxide, unchanged material and resinous products were obtained. **Hydrogenation** of 0.65 g. in ethanol with platinum showed an absorption of one molecule and gave 0.5 g. of dimesitylbutanone-1, X. The compound VII did not give either an oxime or a 2,4-dinitrophenylhydrazone.

**1,4-Dimesitylbutanone-1, X.**—One gram of the chloro ketone VIII was reduced with platinum catalyst in 20 cc. of ethanol, absorbed one molecule of hydrogen, and gave 0.66 g. of purified product melting at 105–105.5° (corr.). Similarly 0.65 g. of dimesityl-2-butenone-1, VII, absorbed one molecule of hydrogen and gave 0.5 g. of purified material melting at 105–105.5° (corr.).

*Anal.* Calcd. for $C_{22}H_{28}O$: C, 85.7; H, 9.2. Found: C, 85.8; H, 9.3.

**1,4-Dimesitylbutanol-1, XI,** was prepared by reducing dimesityl-2-butenone-1, VII, in the usual way by sodium and alcohol under nitrogen. In a similar reduction of 1.6 g. of dimesitylbutanone-1, X, 1.4 g. of nearly pure product was obtained. It was crystallized from ethanol and melted at 147.5–148° (corr.).

*Anal.* Calcd. for $C_{22}H_{30}O$: C, 85.0; H, 9.7. Found: C, 85.3; H, 9.8.

Oxidation of 0.1 g. in 3 cc. of concd. acetic acid with a slight excess of chromic acid in sulfuric acid, warming gently, gave a crude product from which 0.03 g. of crystals which melted at 102° was obtained and identified as dimesitylbutanone-1.

**1,4-Dimesitylbutanone-2, XV.**—This compound was prepared by tin-hydrochloric acid reduction of dimesityl-1,2,4-butanetrione enol, XII, or dimesityl-4-hydroxybutanedione-1,3, XIII. In the former case considerable amounts of di-(trimethylbenzoyl)-ethane was found as well and formed a constant crystallizing mixture with XV which melted at 105–106°. When XIII was used as the starting material, no di-(trimethylbenzoyl)-ethane was formed. This proved to be the best method of preparation, despite the extra step involved, because it avoided the necessity of a laborious separation of the product from IV.

In a typical experiment a mixture of 2.6 g. of XIII, 25 cc. of concd. acetic acid, 20 cc. of concd. hydrochloric acid, and 10 g. of tin, was refluxed for nine hours. The solution was decanted and diluted with water, an oil separating which crystallized. The yield of crude material of m. p. 110–115° was 2.2 g. It was crystallized from ligroin; m. p. 118–119° (corr.).

*Anal.* Calcd. for $C_{22}H_{28}O$: C, 89.7; H, 9.2; mol. wt., 308. Found: C, 85.6; H, 9.3; mol. wt., 304.

Heating with the iodine–phosphorus–acetic acid reagent, with sodium methylate, or with 85% phosphoric acid, was without effect on the compound. A **2,4-dinitrophenylhydrazone** was obtained in the usual way and crystallized from ethyl acetate–ethanol mixtures and from acetone; m. p. 187.5–188° (corr.) (yellow).

*Anal.* Calcd. for $C_{28}H_{32}O_4N_4$: N, 11.5. Found: N, 11.4.

The **semicarbazone** was obtained as colorless crystals by refluxing for twenty-four hours a methanol solution of XV with semicarbazide hydrochloride and sodium acetate; m. p. 177.5–178° (corr.).

*Anal.* Calcd. for $C_{23}H_{33}ON_3$: N, 11.5. Found: N, 11.6.

The **oxime** was prepared by heating an ethanol solution of XV, hydroxylamine hydrochloride, and sodium acetate for two hours. It crystallized from methanol; m. p. 154.5–155.5° (corr.).

*Anal.* Calcd. for $C_{22}H_{29}ON$: N, 4.3. Found: N, 4.6.

**1,4-Dimesitylbutanol-2, XVI.**—Four-tenths gram of dimesitylbutanone-2 was reduced with 2 g. of sodium and 25 cc. of absolute ethanol under nitrogen. On diluting with water and distilling under diminished pressure, 0.46 g. of colorless crystals was separated and recrystallized from methanol; m. p. 125.5–126° (corr.).

*Anal.* Calcd. for $C_{22}H_{30}O$: C, 85.0; H, 9.7. Found: C, 84.7, 84.3; H, 9.8, 9.6.

The **urethan** was prepared by refluxing for eight hours a petroleum ether solution of 0.1 g. of XVI and 0.5 cc. of phenyl isocyanate. On cooling 0.13 g. of product was obtained and crystallized several times from ligroin and from methanol; m. p. 122–122.5° (corr.).

*Anal.* Calcd. for $C_{29}H_{35}O_2N$: N, 3.3. Found: N, 3.3, 2.9.

**1,4-Dimesityl-2-iodobutane, XVII.**—A mixture of 0.2 g. of dimesitylbutanol-2, XVI, 0.05 g. each of iodine and red phosphorus, 8 cc. of concd. acetic acid, 3 drops of water, and 7 drops of hydriodic acid (sp. gr. 1.7) was boiled for two and one-half hours and filtered into a sodium bisulfite solution. The organic material was extracted into ether, freed from acetic acid by washing with sodium hydroxide, and isolated as an oil on evaporation of the solvent. On digestion with ethanol 0.13 g. of crystals was obtained which was recrystallized from absolute ethanol and melted at 105.5–106° (corr.).

*Anal.* Calcd. for $C_{22}H_{29}I$: C, 62.9; H, 7.0. Found: C, 62.8; H, 7.1.

## Summary

The preparations and proof of structures of dimesitylbutanones-1 and -2 and the corresponding monohydric alcohols are described.

In the preparation of dimesitylbutanone-1 the two possible unsaturated ketones were obtained and their structures demonstrated.

CHARLOTTESVILLE, VA. RECEIVED JANUARY 18, 1938

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

# 2,5-Dimesityl- and 2,5-Di-(bromomesityl)-furans

BY ROBERT E. LUTZ, ELIZABETH C. JOHNSON AND JOHN L. WOOD

2,5-Diarylfurans generally can be made by dehydration of the 1,4-diaroyl-1,4-diketones with acetic anhydride and sulfuric acid, although occasionally substituents on the chain hinder the reaction.[1] Few dimesityl compounds have been considered in this connection, however. Acetoxydimesitylfuran is obtainable by the action of acetic anhydride and sulfuric acid on di-(trimethylbenzoyl)-hydroxyethane,[2] and 2,5-dimesityl-3,4-dimethylfuran is formed with exceptional ease from the corresponding saturated 1,4-diketone by this method.[3] Furan ring closure is the chief result in zinc–acetic acid reduction of both *cis* and *trans* di-(trimethylbenzoyl)-dimethylethylenes,[3] a type of reaction which has been observed in relatively few cases[4] and which does not occur in the reduction of di-(trimethylbenzoyl)-ethylene itself.

The dimesityl- and di-(bromomesityl)-1,4-diketones, I and VII, which are unsubstituted on the chain, do not undergo furan ring closure under the usual conditions with acetic anhydride or acetyl chloride and sulfuric acid. Di-(trimethylbenzoyl)-ethane, I, undergoes slow dehydration when subjected to the prolonged action of boiling hydrochloric acid and acetic acid mixtures, to give dimesitylfuran, IV, but the reaction is difficult to bring to completion and is therefore unsatisfactory as a method of preparation. Heating directly with 85% phosphoric acid gives only traces of the furan but brings about chiefly fission of the molecule to mesitylene and succinic acid, a type of reaction which is characteristic of mesitylenic ketones.[5] Both

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(1) *Cf.* the dibenzoyldibromoethanes, Lutz, THIS JOURNAL, **48**, 2916 (1926).

(2) Lutz and Wood, *ibid.*, **60**, 229, 705 (1938).

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

(4) Lutz, *ibid.*, **51**, 3008 (1929).

(5) *Cf.* Klages and Lickroth, *Ber.*, **32**, 1549 (1899); Klages, *ibid.*, **37**, 924, 1715 (1904).