	B. p., °C.	Mm.	M. p., °C.	d^{20}_{20}
1			105–106	
2			59–60	
3	172–173	11		1.082
4			94–95	

The acetate and benzoate were recrystallized from 95% alcohol, the propionate from 60% alcohol.

The acetate, propionate, and benzoate were insoluble in water, sparingly soluble in methyl and ethyl alcohols and readily soluble in benzene, acetone, ether, chloroform, carbon tetrachloride and carbon disulfide. The butyrate differed in that it was also readily soluble in methyl and ethyl alcohols.

Preparation of Tribromomethyl-*p*-tolylcarbinol.—From a mixture of 40 g. of *p*-tolualdehyde, 130 g. of bromoform and 4 g. of potassium hydroxide a yield of 32 g. was obtained. It boiled at 183–186° at 4 mm. and was difficult to distill without undue decomposition. It crystallized on standing and on recrystallization from 6 *N* acetic acid melted at 61–62°.

It is insoluble in water but readily soluble in ethyl alcohol, methyl alcohol, benzene, acetone, ether, chloroform, carbon tetrachloride and carbon disulfide.

Anal. Calcd. for $C_9H_9OBr_3$: Br, 64.31. Found: Br, 64.28.

ESTERS OF TRIBROMOMETHYL-*p*-TOLYLCARBINOL

		M. p., °C.	Formula	Analyses for Br, % Calcd.	Found
1	Acetate	149–150	$C_{11}H_{11}O_2Br_3$	57.81	57.63
2	Propionate	170	$C_{12}H_{13}O_2Br_3$	55.90	55.83
3	Butyrate	63	$C_{13}H_{15}O_2Br_3$	54.14	53.98
4	Benzoate	126	$C_{16}H_{13}O_2Br_3$	50.28	50.11

These esters were all recrystallized from 95% alcohol. They are all insoluble in water, slightly soluble in ethyl and methyl alcohols and very soluble in benzene, acetone, ether, chloroform, carbon tetrachloride and carbon disulfide.

The average yield of all esters prepared was 85%.

Summary

Trichloromethyl-*m*-chlorophenylcarbinol, tribromomethyl-*m*-chlorophenylcarbinol, trichloromethyl-*p*-tolylcarbinol, and tribromomethyl-*p*-tolylcarbinol, as well as their acetic, propionic, butyric and benzoic esters, have been prepared and studied.

MISSOULA, MONT. RECEIVED NOVEMBER 15, 1937

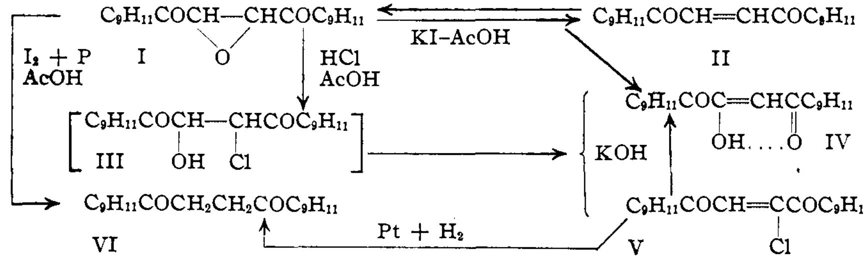
[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA]

Reductions of Di-(trimethylbenzoyl)-ethylene Oxide

BY ROBERT E. LUTZ AND JOHN L. WOOD

This investigation was made because of interest in the effect of substitution of mesityl groups for phenyls on the reactivity of the unsaturated 1,4-diketones and related systems. As was anticipated, many reactions of di-(trimethylbenzoyl)-ethylene oxide are similar or parallel to those of the diphenyl analog which have been described in preceding papers.[1]

Di-(trimethylbenzoyl)-ethylene oxide (I) can be prepared easily in the usual way by the action of sodium peroxide on the unsaturated 1,4-diketone, II.



Attempts to convert the oxide into a chlorohydrin (as was done in the dibenzoyl series) were unsuccessful. Under the usual reaction conditions dimesitylbutanetrione enol IV was obtained, but there was produced in addition small amounts of di-(trimethylbenzoyl)-chloroethylene, V, the structure of which was shown by analysis, hydrolysis to the enol IV, and reduction to di-(trimethylbenzoyl)-ethane, VI. Undoubtedly the chlorohydrin III is formed in these reactions, but it is evidently less stable than the diphenyl analog and decomposes spontaneously in the two possible ways with loss of hydrogen chloride or water. In this connection it is significant that di-(trimethylbenzoyl)-chloroethane, VII, is distinctly less stable than the dibenzoyl analog and easily loses hydrogen chloride to give the unsaturated 1,4-diketone II.

Reduction of the oxide (I) with potassium io-

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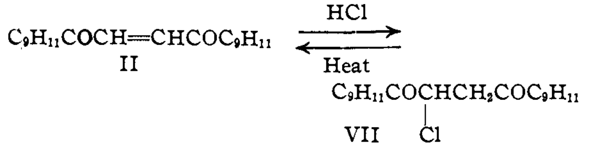
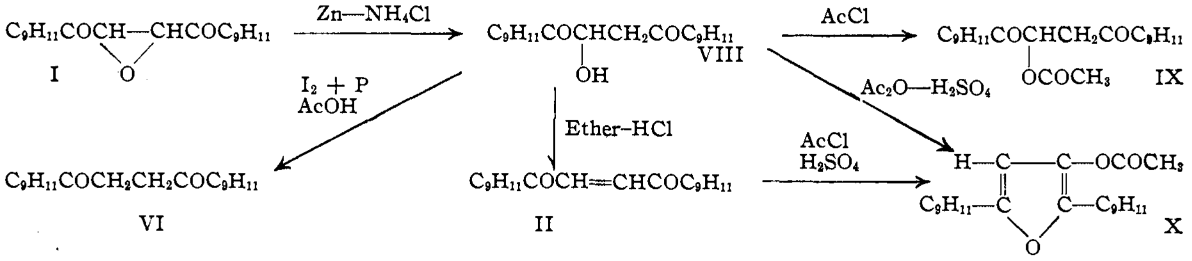
[1] Lutz and Wilder, THIS JOURNAL, **56**, (a) 1987, (b) 2065 (1934).



dide in concd. acetic acid eliminates the oxido oxygen to give the unsaturated 1,4-diketone II, a characteristic reaction[2] which has been applied also to dibenzoylethylene oxide[3] where it proceeds with greater ease and with better yields (along with this reaction in the dimesityl series there occurs also some rearrangement to dimesitylbutanetrione enol, IV). Reduction of the oxide (I) with iodine and phosphorus in acetic acid likewise eliminates the oxido oxygen but carries the reduction further to give the saturated 1,4-diketone, di-(trimethylbenzoyl)-ethane, VI.

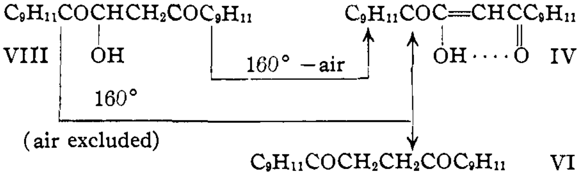


Reductions of di-(trimethylbenzoyl)-ethylene oxide with the metal combination zinc–ammonium chloride–ethanol brings about the expected fission of the oxide ring, and gives as the chief product di-(trimethylbenzoyl)-hydroxyethane, VIII, together with a small amount of an isomer (the latter, described in the experimental part, may be the stereoisomer of XIII, but we have not yet succeeded in proving its structure).

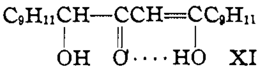
Di-(trimethylbenzoyl)-hydroxyethane is not easily reduced further under the conditions involved in the above preparation. It is distinctly more stable in this respect than the analogous dibenzoylhydroxyethane, $C_6H_5COCH(OH)CH_2COC_6H_5$, which is obtained in the reduction of dibenzoylethylene oxide under relatively mild conditions and is reduced to dibenzoylethane easily with elimination of the hydroxyl group.

The structure of di-(trimethylbenzoyl)-hydroxyethane (VIII) is evident from its reactions. It is converted readily by the iodine–phosphorus–acetic acid reagent into di-(trimethylbenzoyl)-ethane, VI. It is dehydrated to the unsaturated 1,4-diketone II by the action of ethereal hydrogen chloride. It is converted by means of acetyl chloride into a monoacetyl derivative, IX, and by means of acetic anhydride and sulfuric acid into acetoxydimesitylfuran, X. The latter compound is obtainable also directly from di-(trimethylbenzoyl)-ethylene, II, by the action of acetyl chloride and sulfuric acid.

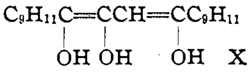
When di-(trimethylbenzoyl)-hydroxyethane is heated directly at high temperature or with alcoholic alkali, in the presence of air, oxidation occurs and dimesitylbutanetrione enol is the chief product (in a few experiments, not duplicated, di-(trimethylbenzoyl)-ethylene was formed through dehydration). If air is excluded during these reactions, however, disproportionation occurs with the formation of dimesitylbutanetrione enol IV and di-(trimethylbenzoyl)-ethane[4] VI.



The isomeric acyloin, dimesityl-4-hydroxy-1,3-butanedione enol, XI,[5] also is easily oxidized or disproportionated under these conditions and gives the same products, IV and VI.



$C_9H_{11}\underset{OH}{CH}-\underset{O}{\overset{\|}{C}}CH{=}\underset{HO}{C}C_9H_{11}$ XI



$C_9H_{11}\underset{OH}{C}{=}\underset{OH}{C}CH{=}\underset{OH}{C}C_9H_{11}$ XII

These reactions probably involve equilibrium between VIII, XI, and the hypothetical tri-enol XII, the latter reacting with oxygen (like ascorbic acid) to give the triketone enol IV. In the absence of air the hydroxyethane VIII probably undergoes spontaneous dehydration to the unsaturated 1,4-diketone II which acts as the oxidizing agent and is reduced to di-(trimethylbenzoyl)-ethane.

The hydrogenation of di-(trimethylbenzoyl)-ethylene oxide with Raney nickel catalyst gives a

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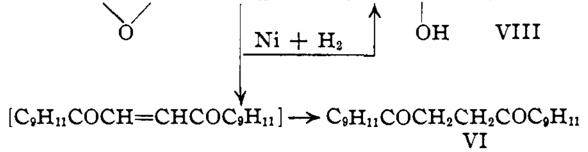
[2] *Cf.* Bodforss, *Ber.*, **49**, 2795 (1916).

[3] Unpublished results, carried out at Emory University by Dr. F. N. Wilder and Miss Katherine Owen.

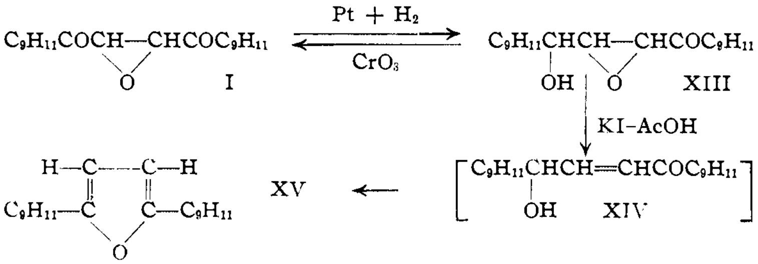
[4] *Cf.* Weinstock and Fuson, THIS JOURNAL, **58**, 1986 (1936).

[5] To be described in a later paper.

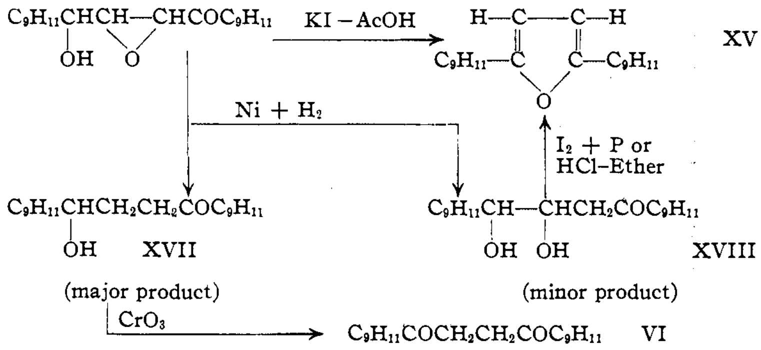
mixture of approximately equal amounts of di-(trimethylbenzoyl)-ethane, VI, and the hydroxy derivative, VIII. The two products are formed independently and are not further acted upon by the reagents. They are, therefore, produced by two competing processes, one the direct reductive fission of the oxide ring, and the other presumably reductive elimination of the oxido oxygen and hydrogenation of the double bond thus produced,[1b] as pictured in the following diagram



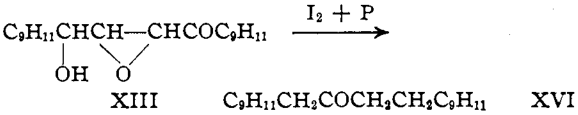
Hydrogenation of carefully purified oxide (I) with a relatively large amount of platinum catalyst in alcohol as solvent, stopped with the addition of approximately one molecule and gave a compound isomeric with di-(trimethylbenzoyl)-hydroxyethane, which proved to be dimesityl-2,3-epoxy-4-hydroxybutanone-1, XIII. This reaction involves simple reduction of one carbonyl to carbinol.



The structure of the reduction product, XIII, is evident from its various reactions. It forms a monourethan and is therefore a monohydric alcohol. It reacts with the calculated amount of chromic acid, regenerating di-(trimethylbenzoyl)-ethylene oxide, showing that the oxido group is intact. With potassium iodide in acetic acid, dimesitylfuran is obtained, formed obviously through loss of the oxido oxygen under relatively mild reducing conditions, with subsequent rearrangement and dehydration of the expected and hypothetical intermediate unsaturated hydroxyketone XIV.



The action of iodine and phosphorus on the new hydroxyoxido ketone, XIII, produces dimesitylbutanone-2, XVI,[5] and very small amounts of a new enolic compound which has not yet been investigated because of lack of material. Possibly the reaction proceeds through rearrangement to an α-diketone or its enol, from which the dimesitylbutanone-2 might well be expected as the final reduction product.



Reduction of the hydroxyoxido ketone XIII was brought about by hydrogenation with Raney nickel catalyst. Nearly two equivalents of hydrogen were absorbed, and the major product (of two) proved to be the expected dimesityl-4-hydroxybutanone-1, XVII, the structure of which was proved by oxidation to di-(trimethylbenzoyl)-ethane, VI. The hydroxy ketone presumably is formed through reductive elimination of the oxido oxygen and subsequent reduction of the double bond produced.

The minor product in this reduction was shown by analysis to be a dihydro compound. The structure XVIII has been assigned since this is consistent with both analysis and expectation, but it has not been rigorously established. The compound is converted into dimesitylfuran, XV, by the iodine–phosphorus reagent, a reaction similar in some ways to the formation of the furan by the action of potassium iodide and concd. acetic acid on the hydroxyoxido ketone itself. The furan, XV, is formed also when XVIII is treated with ethereal hydrogen chloride.

It is interesting to note in connection with these results that apparently Raney catalyst hydrogenations of both di-(trimethylbenzoyl)-ethylene oxide and dimesityl-2,3-epoxy-4-hydroxybutanone-1 (XIII) take place in the same characteristic way, partly with fission of the oxide ring and partly with reductive elimination of the oxido oxygen, to give consistently two independent end-products. In neither case are the groups in the 1- and 4-positions affected. With platinum catalyst, however, the oxide ring is not touched but there is brought about direct reduction of one of the two carbonyl groups.

Experimental Part

***trans*-1,2-Di-(2,4,6-trimethylbenzoyl)-ethylene, II,** was prepared by the Friedel and Crafts reaction with fumaryl chloride and mesitylene.[6] When it was treated with acetic anhydride and varying amounts of sulfuric acid, and heated, considerable amounts were recovered and only non-crystalline products were formed from which no acetoxydimesitylfuran, X, could be isolated. Phosphorus pentachloride reacted with it slowly at 100–120° but only small amounts of unchanged material and resinous products were obtained.

3-Acetoxy-2,5-dimesitylfuran, X.—Two drops of concd. sulfuric acid were added to a suspension of 4 g. of di-(trimethylbenzoyl)-ethylene in 11 cc. of acetyl chloride. Immediate darkening ensued with solution of the suspended solid. The mixture was heated for several minutes on the water-bath, decomposed in ice water, and neutralized with sodium carbonate. Extraction with ether gave an oil which solidified on standing. From this colorless crystals were obtained on crystallization from methanol; m. p. 100–101° (corr.).

Anal. Calcd. for $C_{24}H_{26}O_3$: C, 79.5; H, 7.2; $COCH_3$, 11.9. Found: C, 79.9, 79.4, 79.6; H, 7.3, 7.6, 7.2; $COCH_3$, 8.0.

Some of the saturated and unsaturated dimesityl 1,4-diketones (for example VIII) are converted readily into furans, but others such as VI react in this way only under special conditions. We were unable to convert di-(trimethylbenzoyl)-ethylene into a chlorofuran by means of the usual combination of acetyl chloride and sulfuric acid; under these conditions we obtained instead acetoxydimesitylfuran which, curiously enough, could not be made using the customary acetic anhydride. Dimesitylfuran[5] is not obtainable by dehydration of di-(trimethylbenzoyl)-ethane under the usual conditions with acetyl chloride or acetic anhydride and sulfuric acid, in contrast with dimesityldimethylfuran which is easily obtained from the corresponding saturated 1,4-diketone by this means. The dimesitylfuran may be prepared in good yield, however, by the action of hydriodic acid directly on the saturated or unsaturated 1,4-diketone or on the oxide (I).[7]

1,2-Di-(2,4,6-trimethylbenzoyl)-chloroethane, VII.—Considerable difficulty was encountered in preparing this compound and in duplicating the results. The compound is unstable and readily loses hydrogen chloride during recrystallizations, regenerating the unsaturated 1,4-diketone. A successful experiment (which we were unable to duplicate in several subsequent attempts) is as follows: 5 g. of di-(trimethylbenzoyl)-ethylene was dissolved in 50 cc. of boiling concd. acetic acid and the mixture cooled. Dry hydrogen chloride was passed through the mixture for fifty hours, the suspended material dissolving slowly. On subsequent dilution with water an oil separated. This, upon digestion with petroleum ether, gave a colorless solid which melted at 74°, solidified and remelted at 130°. It crystallized from ethanol but under these conditions considerable amounts of di-(trimethylbenzoyl)-ethylene were produced.

Anal. Calcd. for $C_{22}H_{25}O_2Cl$: Cl, 9.9. Found: Cl, 10.0, 10.1.

Attempts to prepare this compound using alcohol, ether or chloroform, saturated with hydrogen chloride, failed. When the chloroethane was heated at 100°, or refluxed in ethanol for twelve hours, it was transformed into di-(trimethylbenzoyl)-ethylene which was recovered and identified.

1,2-Di-(2,4,6-trimethylbenzoyl)-ethylene Oxide, I.—A suspension of 25 g. of di-(trimethylbenzoyl)-ethylene in 400 cc. of boiling ethanol was cooled to 65°. To this was added, with mechanical stirring, 32 cc. of 30% hydrogen peroxide, followed by 32 cc. of 10% sodium hydroxide. Stirring was continued for ten minutes. The solution was then cooled and seeded, the oxide crystallizing; yield 22 g. (84%). It was recrystallized from methanol or ligroin; m. p. 73.5–74.5° (corr.). It distilled in the vacuum oven at 130° without decomposition.

Anal. Calcd. for $C_{22}H_{26}O_2$: C, 78.5; H, 7.2. Found: C, 78.3; H, 7.1.

Acetyl chloride and sulfuric acid (warmed) were without effect on the oxide. Phosphorus pentachloride at slightly above room temperature converted it into resinous products.

Rearrangement of Di-(trimethylbenzoyl)-ethylene Oxide.—A solution of the oxide in ether, saturated with dry hydrogen chloride at 0°, and allowed to stand for six days, gave largely the enol, IV. With boiling sodium methylate solution the rearrangement was effected but in poorer yield. In concd. acetic acid, saturated with dry hydrogen chloride (standing one week) or in ethanol or methanol with varying concentrations of water and hydrogen chloride, mixtures were obtained of the enol IV and the chloroethylene V which were separated by taking advantage of the acidity of the enol. Because of the formation of the chloroethylene in these reactions, the method was unfavorable for the preparation of the enol.

1,2-Di-(trimethylbenzoyl)-chloroethylene, V.—Dry hydrogen chloride was bubbled through a refluxing solution of the oxide I in 92% ethanol for twelve hours. The enol

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[6] Conant and Lutz, THIS JOURNAL, **45**, 1306 (1923).

[7] Conditions for the preparation of dimesitylfuran in good yield have been developed by Miss E. C. Johnson in this Laboratory.

IV was extracted from the precipitate by shaking a petroleum ether solution of the mixture with sodium carbonate solution. From the petroleum ether a small amount of yellow crystals was obtained and recrystallized from ethanol; m. p. 113–113.5° (corr.); yield 25%.

Anal. Calcd. for $C_{22}H_{23}O_2Cl$: C, 74.5; H, 6.6; Cl, 10.0. Found: C, 74.3; H, 6.8; Cl, 10.2.

The chloroethylene in ethanol with platinum and hydrogen absorbed two moles of hydrogen and gave di-(trimethylbenzoyl)-ethane, VI. When treated with boiling 50% methanol–15% sodium hydroxide the sodium salt of the enol IV was produced in good yield.

Reductions of 1,2-Di-(2,4,6-trimethylbenzoyl)-ethylene Oxide.—Chromous chloride and sodium hydrosulfite were without effect on the oxide.

(a) **Potassium Iodide and Acetic Acid.**—A solution of 0.2 g. of the oxide and 0.2 g. of potassium iodide in 5 cc. of concd. acetic acid was refluxed for two hours. Iodine was liberated. The solution was poured into water containing sodium bisulfite and the precipitated material collected on a filter (yield 0.14 g.). The solid was dissolved in ether and shaken out with aqueous sodium hydroxide, a small amount of the sodium salt of dimesitylbutanetrione enol precipitating. The ether solution gave a small yield of di-(trimethylbenzoyl)-ethylene which was identified by mixed melting point.

(b) **Iodine and Phosphorus.**—A mixture of 0.5 g. of iodine, 0.5 g. of red phosphorus and 25 cc. of 98% acetic acid was heated to boiling and 2 g. of di-(trimethylbenzoyl)-ethylene oxide was added. After two and a half hours of refluxing the hot solution was filtered and poured into 250 cc. of water containing sodium bisulfite. The precipitate was recrystallized from methanol, giving 1.1 g. of nearly pure di-(trimethylbenzoyl)-ethane which was identified by mixed melting point after further purification by crystallization from ligroin.

(c) **Catalytic Reduction.**—No reduction occurred using palladium or barium sulfate as catalyst in ethyl acetate as solvent.

Reduction with platinum in ethanol gave 1,4-dimesityl-4-hydroxy-2,3-epoxybutanone-1 (see discussion under this compound).

Raney nickel catalyst with ethanol as solvent brought about reduction to di-(trimethylbenzoyl)-ethane and di-(trimethylbenzoyl)-hydroxyethane (see discussion under the latter compound).

(d) **Zinc–ammonium chloride–ethanol reduction** gave di-(trimethylbenzoyl)-hydroxyethane together with a second and minor product believed to be a stereoisomer of XIII.

Two grams of the oxide I in 80% ethanol or methanol with 0.5 g. of ammonium chloride was stirred mechanically and treated with an excess of zinc dust at 40–45° for one hour. The mixture was filtered, diluted with water, acidified, and extracted with ether. The oil obtained was crystallized from ethanol and proved to be the hydroxyethane VIII (m. p. 82–87°). Usually in the first crop there came down the higher melting by-product, an isomer, which when pure melted at 119.5–120° and has been termed the "120° compound." It is the less soluble of the two products and crystallizes much more readily than the hydroxyethane. In some experiments this "120° compound" crystallized first directly after removal of the zinc dust by filtration of the hot mixture. When the mixture was filtered directly without first heating, the "120° compound" usually was carried down with the zinc dust and could be extracted by means of ether or boiling ethanol.

The samples of di-(trimethylbenzoyl)-hydroxyethane from these reductions were very hard to free from small amounts of the less soluble higher melting isomer.

In one experiment the crude solid products were subjected to distillation in the vacuum oven, and among the products a 6% yield of di-(trimethylbenzoyl)-ethylene was isolated from the semi-solid distillate and identified. It must have been formed through pyrolytic decomposition of di-(trimethylbenzoyl)-hydroxyethane.

(e) **Zinc and concd. acetic acid reduction,** carried out in the usual way at 50° for one hour, gave oils from which, upon crystallization from ethanol, small amounts of oxide were recovered. From the filtrates in two instances small yields of di-(trimethylbenzoyl)-hydroxyethane were isolated.

(f) **Sodium and alcohol reduction,** carried out in the usual way, gave yields of about 50% of crude dimesitylbutane-1,4-diol which was purified and identified.[6] The low-melting fractions probably were mixtures of this compound and its stereoisomer.

1,2-Di-(2,4,6-trimethylbenzoyl)-hydroxyethane, VIII.—This compound was best prepared by the reduction of the oxide with Raney nickel catalyst. A mixture of 10 g. of the oxide in 200 cc. of 95% ethanol and a sample of the nickel catalyst was shaken with hydrogen, the reduction stopping after about 1.5 molecules had been absorbed. The product was fractionally crystallized and separated into 1.2 g. of nearly pure di-(trimethylbenzoyl)-ethane and 4.3 g. of di-(trimethylbenzoyl)-hydroxyethane melting at 88–90°. A trace of di-(trimethylbenzoyl)-ethylene was found in the mother liquors and probably was formed by dehydration of a small amount of the hydroxyethane.

The hydroxyethane (like dibenzoylhydroxyethane) crystallizes very slowly from solvents. The compound could best be identified by conversion to the acetate. After repeated crystallizations from ethanol it melted at 91–92° (corr.).

Anal. Calcd. for $C_{22}H_{26}O_3$: C, 78.1; H, 7.8. Found: C, 78.1; H, 7.7.

Reactions of Di-(trimethylbenzoyl)-hydroxyethane.—The acetate, di-(trimethylbenzoyl)-acetoxyethane, IX, was obtained in excellent yield by allowing a solution of the hydroxyethane VIII in acetyl chloride to stand at room temperature for forty-five minutes. It was recrystallized from ethanol and melted at 85.5–87.5°.

Anal. Calcd. for $C_{24}H_{28}O_4$: C, 75.8; H, 7.4; $COCH_3$, 11.3. Found: C, 75.8; H, 7.4; $COCH_3$, 11.4.

Conversion to acetoxydimesitylfuran, X, was accomplished by treating the hydroxyethane VIII with acetic anhydride and a few drops of concd. sulfuric acid at room temperature.

The Action of Alkali.—In one experiment (which we were unable successfully to repeat) 0.5 g. of the hydroxyethane VIII in boiling methanol was treated dropwise with 5% aqueous sodium hydroxide. On cooling 0.3 g. of di-(trimethylbenzoyl)-ethylene crystallized and was identified. Repetition of the experiment under similar conditions gave a mixture consisting largely of dimesitylbutanetrione enol together with a small amount of di-(trimethylbenzoyl)-ethane, but no di-(trimethylbenzoyl)-ethylene was detected.

Pyrolysis for fifteen minutes at 160° or at 180–190° in the presence of air gave a mixture which on distillation in the vacuum oven was found to consist largely of dimesitylbutanetrione enol, IV, which was isolated and identified. When the pyrolysis was carried out under diminished pressure (heating first under reflux at 160° until the mixture was yellow), the distillate was found to be a mixture of almost equal amounts of dimesitylbutanetrione enol and di-(trimethylbenzoyl)-ethane.

Reduction.—Zinc and conc. acetic acid at 35–40° (fifteen minutes) was without effect on the hydroxyethane.

A mixture of 0.05 g. of the hydroxyethane, iodine and red phosphorus and 98% acetic acid was refluxed for forty-five minutes. When worked up in the usual way 0.04 g. of di-(trimethylbenzoyl)-ethane was obtained and identified by mixed melting point.

Dehydration was effected indirectly as follows. A stream of dry hydrogen chloride was passed through a solution of the hydroxyethane VIII in dry ether. The solution was allowed to stand overnight and the solvent evaporated. The residue was fused and then crystallized from ethanol, giving di-(trimethylbenzoyl)-ethylene in good yield.

The **compound melting at 120°** (possibly a stereoisomer of **1,4-dimesityl-2,3-epoxy-4-hydroxybutanone-1, XIII**), obtained in 4–16% yields in the above described reduction of the oxide by means of zinc, ammonium chloride and ethanol, was purified by repeated crystallization from ethanol and melted at 119.5–120° (corr.).

Anal. Calcd. for $C_{22}H_{26}O_3$: C, 78.1; H, 7.8. Found: C, 78.0, 77.9; H, 7.9, 7.8.

Reactions.—The following were without action on the "120° compound": acetyl chloride, with or without pyridine, bromine in chloroform, permanganate in acetone, and hydroxylamine. The compound did not give a urethan. It was not reduced by platinum and hydrogen in ethanol. It was not affected by potassium iodide or iodine and red phosphorus in concd. acetic acid at refluxing temperature.

Reduction of 0.7 g. with 5 cc. of hydriodic acid (sp. gr. 1.7) for thirty-five hours gave a solid product which crystallized from ethanol as fine needles (yield 0.2 g.); m. p. 117–119°. It was identified as 1,4-dimesityl-2-butanone.[6]

Chromic acid in sulfuric acid, or in concd. acetic acid, with a small amount of sulfuric acid, at 80°, converted the compound largely into non-crystalline products.

Reduction with Raney nickel catalyst in 95% ethanol proceeded slowly, giving a mixture from which a new compound was isolated and purified to the constant melting point, 160° (corr.).

Anal. Calcd. for $C_{22}H_{30}O_3$: C, 77.2; H, 8.8. Found: C, 77.0; H, 8.9.

1,4-Dimesityl-2,3-epoxy-4-hydroxybutanone-1, XIII.—The platinum-hydrogen reduction of the oxide I in ethanol requires carefully purified material since some persistent impurities, presumably peroxides, poison the catalyst and stop the reaction. Absolute ethanol was found superior to 95%. At times second portions of catalyst had to be added to bring the reaction to completion. Relatively large amounts of catalyst were necessary.

In a typical experiment 20 g. of purified oxide in 300 cc. of absolute ethanol was shaken with 1.4 g. of platinum oxide catalyst and hydrogen, one molecule being absorbed in four hours. The product was isolated by evaporating the solvent. On digestion with petroleum ether 15.8 g. of nearly pure product was obtained and from the petroleum ether 0.9 g. of oxide was recovered. In some of the experiments, yields as high as 95% were obtained. It was recrystallized from ethanol and melted at 129.5° (corr.).

Anal. Calcd. for $C_{22}H_{26}O_3$: C, 78.1; H, 7.8. Found: C, 78.3; H, 7.6.

Oxidation of a sample of XIII with concd. acetic acid and chromic and sulfuric acids gave small but significant yields (20%) of the oxide, I, which was identified.

The urethan was prepared by the action of 1 cc. of phenyl isocyanate in 10 cc. of petroleum ether–ligroin mixture (refluxed for eight hours) on 0.2 g. of XIII. Upon cooling 0.17 g. of the urethan was obtained and recrystallized from 80% ethanol; m. p. 155–156° (corr.).

Anal. Calcd. for $C_{29}H_{30}O_4N$: N, 3.17. Found: N, 3.07.

When XIII was treated with potassium iodide and concd. acetic acid (refluxing two hours) under an atmosphere of nitrogen, dimesitylfuran was obtained in 50% yield. Acetyl chloride and sulfuric acid gave a bright blue solution. Acetic anhydride (with and without sulfuric acid) gave oils which could not be induced to crystallize.

The compound XIII was not reduced with zinc and acetic acid under the usual conditions.

Reduction with iodine, red phosphorus, and concd. acetic acid gave a mixture of products from which were isolated a 20% yield of dimesitylbutanone-2 and a 10% yield of a new enolic substance which has not yet been investigated (it is, however, different from the reduction products of dimesitylbutanetrione enol).

Reduction of dimesityl-2,3-epoxy-4-hydroxybutanone-1, XIII, with Raney nickel catalyst, carried out in the usual way on 9.6 g. of material in 150 cc. of 95% ethanol, required twenty-six hours, 1.5 moles of hydrogen being absorbed. Fractional crystallization of the products from ethanol gave 7.2 g. of dimesityl-4-hydroxybutanone-1, XVII (a yield of 75%). From the mother liquors 1.1 g. of nearly pure dimesityl-3,4-dihydroxybutanone-1, XVIII, was obtained, a yield of 11% (in another experiment a yield of 20% of the glycol XVIII was obtained).

1,4-Dimesityl-3,4-dihydroxybutanone-1, XVIII, was obtained as fine needle crystals from carbon tetrachloride and was sublimed in the vacuum oven at 130°; m. p. 162–163° (corr.).

Anal. Calcd. for $C_{22}H_{28}O_3$: C, 77.6; H, 8.2. Found: C, 77.5; H, 8.1.

Oxidation under a variety of conditions with chromic acid and sulfuric acid in concd. acetic acid gave only non-crystalline products.

Conversion to dimesitylfuran in 50% yield was brought about by three hours of refluxing of a mixture of XVIII, red phosphorus, iodine, and 95% acetic acid.

1,4-Dimesityl-4-hydroxybutanone-1, XVII, was obtained as colorless crystals from dilute ethanol; m. p. 132–133° (corr.).

Anal. Calcd. for $C_{22}H_{28}O_2$: C, 81.4; H, 8.6. Found: C, 81.6; H, 8.7.

Oxidation of XVII in concd. acetic acid with chromic acid and sulfuric acid took place readily at room temperature or at 70° and yields of di-(trimethylbenzoyl)-ethane ranging from 10–25% were isolated.

Summary

Di-(trimethylbenzoyl)-ethylene oxide has been prepared and transformed into di-(trimethylbenzoyl)-chloroethylene and dimesitylbutanetrione enol.

Reductions under a variety of conditions are reported. The oxide is converted by means of potassium iodide into di-(trimethylbenzoyl)-ethylene, by the iodine–phosphorus reagent into di-(trimethylbenzoyl)-ethane, by zinc–ammonium chloride into di-(trimethylbenzoyl)-hydroxyethane, by nickel and hydrogen into a mixture of di-(trimethylbenzoyl)-ethane and -hydroxyethane, and by platinum and hydrogen into dimesityl-4-hydroxy-2,3-epoxybutanone-1.

The reactions of di-(trimethylbenzoyl)-hydroxyethane are described, including reduction, dehydration, acylation, conversion to acetoxydimesitylfuran, oxidation and disproportionation.

Dimesityl-4-hydroxy-2,3-epoxybutanone-1 was reduced to dimesityl-4-hydroxybutanone-1 and dimesityl-3,4-dihydroxybutanone-1.

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The Preparation of Acetylaldonic Acids

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The first preparation of a partially acetylated aldonic acid was reported by Upson and Bartz,[1] who found that acetylation of *d*-gluconolactone with zinc chloride and acetic anhydride resulted in rupture of the lactone ring with the formation of tetraacetylgluconic acid monohydrate. In 1936 Major and Cook[2] observed that further acetylation of this compound produced pentaacetylgluconic acid monohydrate, from which pentaacetylgluconic acid itself readily was obtained. These investigators converted the acid to the acid chloride and hydrogenated the latter to aldehydo glucose pentaacetate.

This new synthesis of aldehydo sugars, to be a general reaction, obviously requires a general method for the preparation of fully acetylated aldonic acids. Except for the glucose derivative, the only other such compounds mentioned in the literature are *d*-, *l*-, and *dl*-tetraacetylxylonic acids. These were also prepared by Major and Cook, not by acetylation of a δ-lactone but by oxidation of the corresponding aldehydoxylose tetraacetates. Although a few δ-lactones of aldonic acids are known, the γ-lactones are much more common. For purposes of this synthesis, however, the γ-lactones are unsatisfactory because Upson and Bartz found that γ-lactones undergo acetylation to yield an acetylated lactone, rather than the aldonic acid. They reported also that attempts to acetylate δ-mannonolactone yielded only 2,3,5,6-tetraacetyl-γ-mannonolactone. The method used by Major and Cook, therefore, cannot be regarded as a general one for the synthesis of acetylaldonic acids. Development of a general method for this purpose was the objective of the present work.

A satisfactory means of preparing the acids from the corresponding aldoses has been found through the following sequence of steps: aldose ⟶ aldose oxime ⟶ acetylaldononitrile ⟶ acetylaldonamide ⟶ acetylaldonic acid.

The first two reactions involved, being part of the familiar Wohl method of degradation, have been reported for all the simple aldose sugars. Precedent exists also for the next step inasmuch as the reaction of pentaacetylgluconononitrile with hydrogen bromide in glacial acetic acid has been reported by Zemplén and Kiss[3] to produce pentaacetylgluconamide. This reaction was extended to the acetylated nitriles of *d*-galactose, *d*-xylose, and *l*-arabinose. In each instance, a satisfactory yield of the corresponding acetylaldonamide was obtained.

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[1] Upson and Bartz, THIS JOURNAL, **53**, 4226 (1931).

[2] Major and Cook, *ibid.*, **58**, 2410, 2474 (1936).

[3] Zemplén and Kiss, *Ber.*, **60**, 165 (1927).