

For characterization the aceto compound (0.15 g.) was refluxed in alcohol (10 cc.) and acetic acid (5 drops) with 2,4-dinitrophenylhydrazine (0.2 g.). The product separating in bright yellow crystals (0.24 g.) proved to be a mixture of stereoisomers present in about equal amounts. Fractional crystallization from alcohol gave orange plates, m. p. 122–124°, and yellow needles, m. p. 135–136°, of the isomeric 2,4-dinitrophenylhydrazones.

*Anal.* Calcd. for  $C_{12}H_{14}O_6N_4$ : C, 48.98; H, 4.79; N, 19.04. Found, plates: C, 48.92; H, 4.73; N, 18.89. Found, needles: C, 48.92; H, 4.59; N, 18.75.

**Action of Alkali on  $\alpha$ -Acetotetrahydrofuran.**—The ketone (2 g.) was refluxed for two hours with 16 cc. of alcohol and 4 cc. of 10 *N* sodium hydroxide, 10 cc. of alcohol was added to the two-phase, dark red mixture and refluxing was continued for two hours. After removing the alcohol at reduced pressure the alkaline liquor was extracted with ether. Distillation gave a small fraction (0.35 g.) of colorless liquid of b. p. close to that of the starting material (61–63° at 10 mm.). The remainder was a dark red oil which did not distil to an appreciable extent up to 190° (8 mm.). In another experiment the proportion of red oil was about the same after refluxing for only one hour. This oil seemed to contain an alcoholic reaction product for there were indications of interaction with dinitrobenzoyl chloride in pyridine and with both phenyl isocyanate and  $\alpha$ -naphthyl isocyanate; the products were obtained only as oils. There was no reaction

with dinitrophenylhydrazine and the reagent was recovered unchanged.

### Summary

Spectrographic evidence confirms the previous indications that anhydrosarsasapogenoic acid contains an  $\alpha,\beta$ -unsaturated carbonyl group and that sarsasapogenoic is a non-conjugated carbonyl compound. Another compound of the sapogenoic acid type has been obtained by the oxidation of sarsasapogenone, and a previously described oxidation product has been recognized as desoxysarsasapogenoic acid. Anhydrotetrahydrosarsasapogenoic acid shows no selective absorption in the ultraviolet and hence does not contain a carbonyl group as previously supposed; a new formula is suggested.

Octahydro- $\alpha,\alpha'$ -difuryl, examined as a possible model for the Tschesche-Hagedorn formulation of the side chain, exhibits sensitivity to acids comparable with that characteristic of the sapogenins. It is considered that this formulation accounts satisfactorily for the acid-specific reactions as well as for the oxidation results.

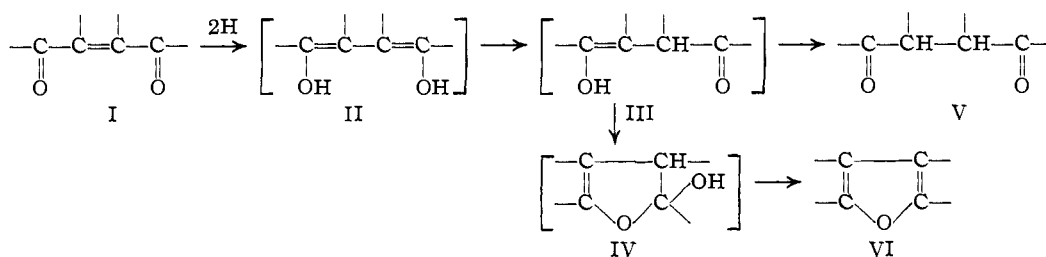
CONVERSE MEMORIAL LABORATORY  
CAMBRIDGE, MASSACHUSETTS RECEIVED MAY 17, 1939

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

## The Mechanism of Reduction of Conjugated Systems with Terminal Carbonyl Groups. Dienols Obtained from Unsaturated 1,4-Diketones<sup>1</sup>

BY ROBERT E. LUTZ AND WILLIAM G. REVELEY

There is definite evidence that reductions of unsaturated 1,4-diketones by means of soluble reducing agents, by metal combinations, and even



by catalytic hydrogen under certain conditions, proceed largely if not exclusively through 1,6-addition of hydrogen or its equivalent at the oxygen atoms with the formation of intermediate dienols (II) which correspond to hydroquinones formed in the reduction of quinones, but which

are unstable and ketonize quickly to the saturated 1,4-diketones (V) or undergo dehydration to the corresponding furans (VI).<sup>2</sup>

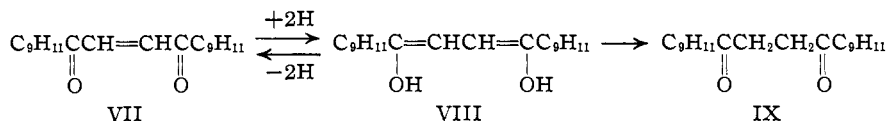
The furans probably are not formed directly from the dienol but rather through rearrangement to the mono-enol III, cyclization to IV, and finally loss of water. In support of this sequence of changes mention should be made of the formation of the furan from the mono-enol produced by 1,4-

(1) This paper was presented at the Baltimore meeting of the American Chemical Society, April 4, 1939.

(2) Cf. (a) Conant and Lutz, *THIS JOURNAL*, **45**, 1047 (1923) (b) Lutz, *ibid.*, **51**, 3008 (1929); (c) Lutz and Palmer, *ibid.*, **57**, 1947 (1935), 1957 (1935).

addition of hydrogen chloride to the  $\alpha,\beta$ -unsaturated ketone system of  $C_6H_5COCH=C(Cl)CO-$

a small amount of added piperidine to catalyze ketonization.



$C_6H_5$ ,<sup>3</sup> and the close analogy for cyclization of the type suggested in the ready formation of hydroxyfuranones from 1,2,4-triketone enols.

It has been shown that reduction of the analogous conjugated system of the  $\alpha$ -diketones with zinc or catalytic hydrogen proceeds 1,4 to give mobile intermediate ene-diols of the type  $RC(OH)=C(OH)R$  which could be fixed and isolated as diacetates.<sup>4</sup> Recently the important discovery that enols of mesityl ketones are extraordinarily persistent and slow to ketonize<sup>5a</sup> has been utilized to demonstrate this mechanism: catalytic reduction of three monomesityl  $\alpha$ -diketones<sup>5b,c</sup> of the type  $C_6H_{11}COCOR$  produces fairly persistent ene-diols which undergo rearrangement to the  $\alpha$ -hydroxy ketones or ready oxidation back to the  $\alpha$ -diketones; and dimesityl diketone is reducible to stereoisomeric metastable crystalline ene-diols.<sup>4b,6</sup> The extraordinary persistence of these ene-diols appears to be at a maximum in compounds such as the dimesityl derivative where the migrating hydrogen must go to a carbon directly linked to a mesityl nucleus.

Further experiments on 1,4-dimesityl unsaturated 1,4-diketones were suggested by the above facts and have been carried out in order to obtain more information concerning reduction of conjugated systems of the type involved and the chemistry of the dienols which are produced.

Hydrogenation of di-(trimethylbenzoyl)-ethylene (VII) in ethanol at 0° with platinum as catalyst takes place rapidly with absorption of one molecule of hydrogen. Di-(trimethylbenzoyl)-ethane (IX) is obtained practically quantitatively when the reaction mixture is allowed to stand for a period of time under hydrogen, preferably with

The dienol VIII was shown to be the chief primary product under these conditions by filtering the solution rapidly under an atmosphere of nitrogen and running it directly into a solution of a known amount of iodine, the unused excess then being determined by titration with standard sodium thiosulfate. Assuming the amount of iodine used up to be a measure of the amount of the dienol present, yields of over 90% were demonstrated in several experiments. The oxidation of the dienol is presumably a 1,6-process and analogous to the oxidation of *p*-hydroquinones.

Reduction of di-(trimethylbenzoyl)-ethylene (VII) by means of zinc and acetic acid, a representative metal combination, ordinarily produces di-(trimethylbenzoyl)-ethane (IX) in good yield. It has been possible to show that here also the chief primary product is the dienol VIII. The reaction was carried out under modified conditions at 0°, and the resulting solution filtered from the zinc directly into iodine solution under an atmosphere of nitrogen; 61% of one mole of iodine was reduced. The dienol is decidedly mobile in the type of solvent used, however, as was shown in catalytic hydrogenations carried out in a somewhat similar solvent combination. Assuming a comparable rate of ketonization during manipulation in the zinc-acetic acid reduction and making due allowance, the result indicates that addition was practically exclusively 1,6, as would be expected.<sup>2a</sup>

In many of the experiments using the iodine oxidation method of analysis of the products of reduction, the results were checked by actual isolation and separation of the mixture of saturated and unsaturated 1,4-diketones. Fractional crystallization, while effective and successful in several instances, was laborious and inaccurate. A rapid and convenient method of separating was developed utilizing the conversion of the unsaturated diketone into the water soluble addition product X by the action of a boiling solution of sodium bisulfite in 60% ethanol; the water soluble sulfonate could be separated easily from the saturated diketone which was recovered and

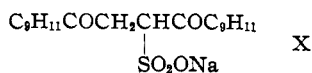
(3) Lutz and Wilder, *THIS JOURNAL*, **56**, 1193 (1934).

(4) (a) Thiele, *Ann.*, **306**, 142 (1899); (b) Thompson, *THIS JOURNAL*, **61**, 1281 (1939).

(5) (a) Kohler, Tishler and Potter, *ibid.*, **57**, 2517 (1935); (b) Kohler and Thompson, *ibid.*, **59**, 887 (1937); (c) Lutz and Wood, *ibid.*, **60**, 705 (1938).

(6) Fuson and Corse, *ibid.*, **61**, 975 (1939). Incidentally, in connection with the above facts, attention may be called to the significant parallels between 1,4-reductions of  $\alpha$ -diketones, pinacol reduction and dimolecular reduction of acid chlorides [cf. Werner, *Chem. Ztg.*, **1**, 4; Erlenmeyer, *J. prakt. Chem.*, **65**, 351 (1902); Klinger, *Ber.*, **24**, 1268, 1271 (1891); **31**, 1217 (1898)], and between the 1,4-oxidation of ene-diols and 1,2-glycols.

weighed, the amount of the unsaturated diketone being determined by difference.

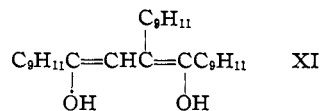


In connection with the mechanism of the main course of reduction in these experiments, 1,2-addition directly at the ethylene linkage, or 1,4-reduction of the  $\alpha,\beta$ -unsaturated ketone grouping with the formation of an intermediate monoenol of the type III, giving intermediate products oxidizable directly or through subsequent enolizations to the unsaturated 1,4-diketone, could not account for the formation of the easily oxidizable dienol and are therefore excluded. Enols and dienols in this series would be unstable and enolization of a carbonyl group during or after reduction would be most unlikely under the conditions of these experiments. Furthermore, there is now evidence in another series for the existence of four substituted monoenols of the type III, one of which has been isolated crystalline; and none of these are oxidizable by air or iodine nor enolized further under ordinary conditions.<sup>7</sup>

Experiments were made to determine the persistence of the dienol (VIII). The best yields were obtained by reduction in ethanol at 0°. Ketonization under these conditions is evidently very slow in spite of the manipulations covering nearly three hours between initiation of hydrogenation and the reaction with iodine. Solutions of the dienol, filtered from catalyst under an atmosphere of nitrogen and allowed to stand quietly at 26–29°, were found to possess a half life period of about twelve hours; however, when shaken at room temperature either in the hydrogenation flask and in the presence of the catalyst, or in another vessel, filtered from catalyst and under an atmosphere of nitrogen, the half life period was considerably less (approximately two hours). The dienol, then, is moderately persistent even though there is no hindering group directly attached to either of the carbons to which the enol hydrogens migrate.

Preliminary attempts to isolate the dienol have not been successful. Attempted reaction with diazomethane brought about ketonization instead. However, a crystalline dienol of this type, namely, XI, melting at 70–71°, has been obtained in the 1,2,4-trimesityl series and will be described in a later report.<sup>7</sup>

(7) Lutz and Kibler, results to be published shortly.



It seemed unlikely that catalytic hydrogen would add 1,6 to unsaturated 1,4-diketones exclusively under all conditions, and an attempt was made to find conditions favoring normal hydrogenation at the ethylene linkage. Of course the conditions tested were necessarily limited to those under which the dienol would likely be persistent. In ethanol solution, temperature has a very marked effect as shown by a typical experiment carried out at room temperature instead of 0°, the time elapsing between initiation of reduction and analysis of the resulting mixture being held to a minimum (seven minutes). The amount of dienol formed, allowing for the small amount of ketonization which would occur during the manipulation, was approximately 30%, in contrast with 90–94% obtained in the experiments carried out at 0°. It is therefore evident that the reduction is more ordered and consistently 1,6 at lowered temperatures.

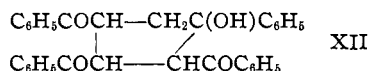
A series of reductions using platinum as catalyst was carried out at 0° in different solvents, the products being analyzed by the iodine oxidation method. The following percentages of dienol were found: in 95% ethanol, 91–94%; in a 4–1 dioxane–ethanol mixture, 90%; in ethyl acetate, 78%; in isopropyl ether, 60%; in benzene (at 5°), 54%; in *n*-hexane, 60%; and in decalin, 17%. These reductions must have proceeded 1,6 at least to the extent of the figures given, and possibly a little more since a small amount of ketonization may have occurred before completion of hydrogenation and analysis of the solution. The amount of ketonization in these solvents at 0° is probably very small and there is no reason to suspect that there would be an abnormally high rate in decalin, the one solvent in which the yield of dienol is very low.

The catalytic reduction of VII in an acetic–propionic acid mixture at 0° gave a yield of dienol on the order of 40–50%. This value is a rough approximation only, because of the mobility of the dienol under these conditions, and was estimated by extrapolation from values determined in several runs in which the time of shaking the reaction mixture was varied.

From the foregoing results it is obvious that conditions have a marked and varied influence on

the mode of catalytic hydrogenation of di-(trimethylbenzoyl)-ethylene, and that there is no consistent solvent effect. The contrasting yields of dienol obtained in *n*-hexane and in decalin are surprising. In the latter solvent when 1,6-addition is at a minimum, 1,2-addition directly at the ethylene linkage is probably the dominant reaction, although of course 1,4-addition is also possible.

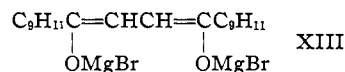
In this connection attention should be called to the effect of solvent and conditions on the yield of cyclic dimolecular products in the catalytic reduction of dibenzoyl ethylene.<sup>2c</sup> In alcohol as one extreme a mechanism involving at least one carbonyl must be involved in view of the large yield of cyclic dimolecular product (XII). On the other hand, when hydrogenation is carried out in decalin as the solvent, complications involving enolic intermediates are at a minimum with normal net hydrogenation at the ethylene linkage predominant. In the case of reduction of the allyl ether system of pseudocodeine types, conditions also have a marked effect on the course of addition, some consistently favoring one mode over another.<sup>8</sup>



This work is being extended to other and longer conjugated systems, including types in which an aromatic nucleus furnishes one or more of the double bonds involved in the system connecting the two carbonyl groups.

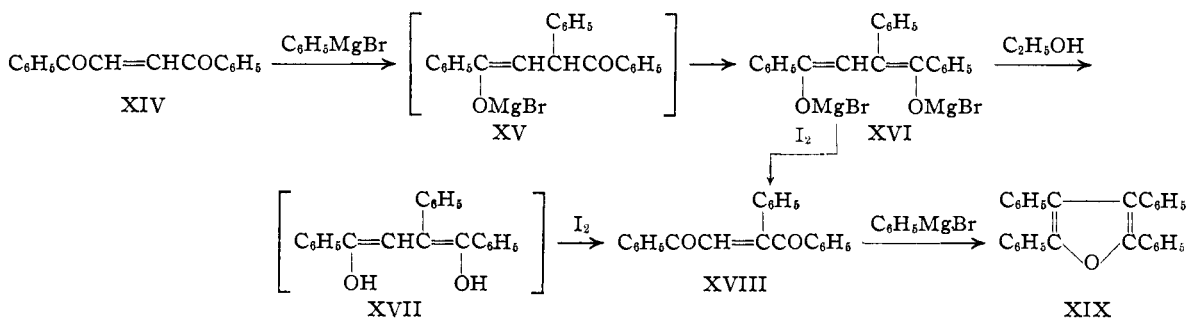
The fact that the dienol produced in reduction of di-(trimethylbenzoyl)-ethylene is sufficiently persistent to permit oxidation back suggested a simple method of converting the 1,4-dimesityl saturated 1,4-diketones into the corresponding unsaturated diketones through hydrolysis of the dimagnesium dienolate under oxidizing conditions. This method is of value because it makes possible

the synthesis of a type of unsaturated diketone which cannot be prepared by the usually convenient nitric acid oxidation of the corresponding furan. In the case of di-(trimethylbenzoyl)-ethane, the dimagnesium dienolate (XIII) is easily made by heating the saturated diketone (IX) with an excess of phenylmagnesium bromide at 110° in isoamyl ether. The mixture, when poured into a precooled solution of iodine in 95% ethanol, gave *trans*-di-(trimethylbenzoyl)-ethylene (VII).



The above procedure has proved useful in the preparation of dimesityl unsaturated diketones with substituents on the ethylene linkage, utilizing the dimagnesium dienolates produced by the action of the Grignard reagent on di-(trimethylbenzoyl)-ethylene.<sup>7,9</sup>

It would be expected that the dienols of ordinary saturated 1,4-diketones such as dibenzoyl ethane would be extremely unstable and would undergo rapid ketonization if formed in any reaction. Nevertheless, it seemed possible that some dienols of this type might exist long enough to be caught by the oxidation reaction. No simple method is available to study the dienol of dibenzoyl ethane and the dimagnesium dienolate has not been made. However, ether solutions of a phenylated analog, namely, the dimagnesium dienolate XVI formed by the addition of phenylmagnesium bromide to dibenzoyl ethylene (XIV), is readily available;<sup>9</sup> when decomposed in cold alcoholic iodine solution *cis*-dibenzoylphenylethylene (XVIII) is obtained and none of the saturated diketone. This result is of particular significance in that it demonstrates in another way the correctness of the mechanism proposed for the action of the aryl Grignard reagents on unsaturated 1,4-diketones.<sup>9</sup>



(8) Lutz and Small, *THIS JOURNAL*, **54**, 4715 (1932).

(9) Lutz and Tyson, *ibid.*, **56**, 1341 (1934).

An interesting result was observed when the ether solution of the dimagnesium dienolate XVI, containing a large excess of phenylmagnesium bromide, was poured into a cooled ether solution of an excess of iodine. Tetraphenylfuran (XIX) was produced. Evidently the dienolate XVI was first oxidized directly to dibenzoylphenylethylene (XVIII), and was then converted into tetraphenylfuran by 1,4-addition of phenylmagnesium bromide followed by the equivalent of dehydration, the latter reactions (known<sup>10</sup>) competing favorably with cleavage of phenylmagnesium bromide by iodine.

### Experimental Part

**The Catalytic Reduction of Di-(trimethylbenzoyl)-ethylene.**—In a number of preliminary experiments an apparatus was devised to carry out hydrogenations at  $-5$  to  $0^\circ$  with an arrangement for manipulating the solution afterward under an inert atmosphere. The hydrogenation flask was immersed in a cooling bath. The main side neck of the flask was fitted with a glass tube slip joint holding a siphon tube with a stopcock; this siphon tube could be pushed down into a small depression blown in the bottom of the flask whereby the solution could be drawn out by suction. A separatory funnel was sealed to the neck of the flask for introduction of solvent. The siphon was connected to a sintered glass funnel and this in turn to a receiving flask arranged for sweeping with nitrogen and for application of suction. The material being reduced was first dissolved in the hot solvent and the solution quickly chilled to produce fine crystals (since the reactions were run at  $0^\circ$  the solid unsaturated diketone was usually present but passed into solution as the hydrogenation proceeded). Completion of the reduction was indicated by the marked slowing down or stopping of hydrogen absorption after approximately one molecule had been used up, and by solution of the unsaturated diketone and discharge of its yellow color. Upon completion of reduction, the siphon was lowered and the solution drawn over by suction, through the sintered glass funnel to remove the catalyst, protected by an atmosphere of hydrogen or nitrogen, into the receiving flask. The hydrogenation flask was then rinsed with several portions of pure solvent. In most of the experiments the receiving flask contained an excess of aqueous or alcoholic iodine (a known amount); the dienol present was oxidized immediately by the iodine, and the unreacted iodine was then determined at leisure by titration with standardized sodium thiosulfate. In some experiments the receiving flask was used as a means of storage for testing the stability of the dienol under certain conditions, and for experiments on the dienol itself, suitable arrangements being made for the introduction of reagents or for the removal of aliquot parts, all under a protective atmosphere of purified nitrogen.

In a number of experiments carried out at room temperature an attempt was made to minimize the time elapsing between initiation of reduction and analysis of the product. A device was used to introduce the catalyst

after arranging and sweeping the apparatus because it was found that hydrogenation started to some extent before shaking was begun. The catalyst was placed in a thin glass bulb blown on the end of a glass tube passing through a rubber stopper into the main side neck of the flask; this was filled with alcohol; the siphon tube, also filled with alcohol, was inserted into the glass bulb through a rubber tube slip joint and served as a plunger; when ready the siphon tube was pressed down breaking the glass bulb and allowing the catalyst to drop into the mixture, shaking being started immediately thereafter.

In several runs with certain batches of catalyst, only small amounts of dienol were obtained and in these instances it was demonstrated that there was present in the catalyst a trace of alkali sufficient to be detectable by indicators in the washings. This trace of alkali was not easily removed. In a typical case a sample of catalyst containing alkali was treated as follows: it was washed, repeatedly with water, then with dilute nitric acid, and again with water; it was dried *in vacuo* at  $200^\circ$ ; it was then washed with dilute ammonium hydroxide and successive portions of water and dried at  $200^\circ$  *in vacuo*, the process being repeated a second time. Only at the end of this treatment was the sample of catalyst free from alkali or acid, giving, when reduced with hydrogen in pure water, an aqueous suspension which was neutral to indicators. This batch of catalyst, though less active than other preparations, brought about reduction of di-(trimethylbenzoyl)-ethylene to the dienol in 90% yield through the usual manipulation. The production of traces of alkali in the catalyst apparently was minimized by lowering the sodium nitrate fusion temperature during the preparation.

The results of a series of experiments under different conditions of temperature, solvent and time, are listed in the table.

SOME TYPICAL CATALYTIC HYDROGENATIONS OF DI-(TRIMETHYLBENZOYL)-ETHYLENE

Solvent	Vol. of solvent per g., <sup>a</sup> cc.	Time, min.	at $^\circ\text{C}$ . (Temp.)	Dienol, <sup>b</sup> % obtained
95% Ethanol	120	7	$-5$ to $0$	31.5
95% Ethanol	120	180	$-5$ to $0$	90.5
95% Ethanol	121	172	$-5$ to $0$	93.7 <sup>c</sup>
95% Ethanol	117	125 <sup>d</sup>	$-5$ to $0$	
		and 2.0 hrs.	26	83.2
		6.3 hrs.	26	65.3
		11.5 hrs.	26	48.4
		20.5 hrs.	26-29	19.0
		35.2 hrs.	26	1.4
95% Ethanol	116	60	$-5$ to $0$	
		and $90^\circ$	24	56.2
Acetic Acid	113	12.5	$-5$ to $0$	30.7
(37% propionic acid) <sup>f</sup>	158	42	$-5$ to $0$	12.9
	123	60	$-5$ to $0$	3.3
Dioxane (20% ethanol) <sup>g</sup>	143	65	$-5$ to $0$	90.3 <sup>c</sup>
Ethyl acetate <sup>h</sup>	116	60	$-5$ to $0$	76.2
Isopropyl ether <sup>i</sup>	128	65	$-5$ to $0$	59.5 <sup>c</sup>
Benzene <sup>i</sup>	135	85	+5	53.5 <sup>c</sup>
<i>n</i> -Hexane <sup>j</sup>	148	120	$-5$ to $0$	59.5
Decalin <sup>k</sup>	167	135	$-5$ to $0$	16.7 <sup>c</sup>

<sup>a</sup> The amount of VII used in each run was 0.5 to 0.6 g. The amount of catalyst (PtO<sub>2</sub>) per gram was 0.15 to 0.30

(10) Hahn and Murray, *THIS JOURNAL*, **36**, 1484 (1914).

g. <sup>b</sup> Determined by iodine oxidation and titration for unused iodine. <sup>c</sup> These results were checked by separation of the products after iodine oxidation, using the sodium bisulfite method, and isolating and weighing the saturated 1,4-diketone (IX). <sup>d</sup> The solution containing the reduction products (largely dienol) was filtered from the catalyst and allowed to stand quietly under an atmosphere of purified nitrogen for the lengths of time and at the temperatures given, aliquot parts then being drawn off and analyzed by the iodine oxidation method. A larger amount of VII was used in this experiment (1.2 g). <sup>e</sup> The solution of reduction products was allowed to come to room temperature; then, without removing the catalyst, the shaking was continued 90 min. <sup>f</sup> 63% by volume of acetic acid. The purpose of adding propionic acid was to lower the freezing point so that the reaction could be run at 0°. <sup>g</sup> 80% by volume dioxane; the ethanol was added to lower the freezing point. <sup>h</sup> Dried over anhydrous sodium sulfate and distilled once. <sup>i</sup> Dried over sodium and distilled twice. <sup>j</sup> A larger amount of catalyst was used here in order to speed up the reaction.

Semi-quantitative checks on many of the determinations of the dienol yields were made as follows: the product, consisting of a mixture of the saturated and the unsaturated diketones (VII and IX), was isolated, dried and weighed. This mixture was then subjected to the action of a boiling 60% ethanol solution containing a large excess of sodium bisulfite until the yellow color of the unsaturated diketone was thoroughly bleached. The mixture was then diluted with water and the precipitate of unreacted di-(trimethylbenzoyl)-ethane was filtered off and weighed. The amount of unsaturated 1,4-diketone was determined by difference and corresponded to the amount of dienol which had been oxidized. In every case indicated in the table the results of the iodine oxidation and titration for unused iodine were checked by this method within a few per cent.

In some cases the absorption of hydrogen was apparently low due to temperature fluctuation in the cooling system or to reduction getting under way before shaking was begun. In several such instances the check analysis by the bisulfite method showed that reduction had actually been complete; if reduction had not been complete the yield of the saturated diketone would have been lower and the yield of unsaturated diketone higher than the values indicated by the iodine oxidation analysis.

**1,4-Dimesitylbutane-1,4-dione-2-sulfonic Acid** (see X).—Two grams of di-(trimethylbenzoyl)-ethylene (VII) and 2 g. of sodium bisulfite were added to 25 cc. of 60% ethyl alcohol and the mixture refluxed on a steam-bath for fifteen minutes. The free sulfonic acid, liberated by pouring the reaction mixture into dilute hydrochloric acid, crystallized out as white plates; it was moderately soluble in water and in ether; the yield was 2.2 g. (88%). It was purified by conversion into the *lead salt* in aqueous medium, using lead acetate, and by repeated crystallization of this from methanol-water mixtures.

*Anal.* Calcd. for  $C_{18}H_{18}O_6S$ : Pb, 20.5. Found: Pb, 20.1.

**Zinc and Acetic Acid Reduction.**—A hot solution of 3 g. of VII in 40 cc. of concd. acetic acid, 40 cc. of diethyl

ether and 1 cc. of water was cooled to  $-5$  to  $0^\circ$ , fine crystals being produced, and 1.5 g. of zinc dust was then added over a period of three minutes. The mixture was shaken for twenty minutes and was filtered and washed directly into cooled alcoholic iodine. The whole operation was carried out under a protective atmosphere of purified nitrogen. Previous experiments had shown that reduction was complete within this time. Analysis for the unused iodine showed 60.9% dienol to have been present at the moment of filtration.

**Preparation of *trans*-Di-(trimethylbenzoyl)-ethylene (VII) from Di-(trimethylbenzoyl)-ethane (IX).**—A sample of IX (0.79 g.) was treated with an excess of methylmagnesium iodide in isoamyl ether and the mixture heated for seventy-five minutes at  $110^\circ$ ; at the end of this time the evolution of methane had ceased, approximately two moles being liberated (collected). The mixture was then poured into a cooled solution ( $0^\circ$ ) of 1.6 g. of iodine in 60 cc. of 95% ethanol. The solvent was removed by distillation and 0.33 g. of VII was recovered (42%).

**Preparation of *cis*-1,2,4-Triphenylbutenedione-1,4 (Dibenzoylphenylethylene) (XVIII) and Tetraphenylfuran (XIX) from Dibenzoylphenylethylene (XIV).**—Four grams of dibenzoylphenylethylene was added to a solution of phenylmagnesium bromide made from 2.5 g. of magnesium and 10 cc. of bromobenzene in 100 cc. of absolute ether. The mixture was refluxed for twenty minutes, cooled to  $0^\circ$ , and poured into 200 cc. of 95% ethanol containing 9 g. of iodine (cooled to the same temperature). After removal of the solvents, a brown oil was obtained from which 0.65 g. of *cis*-dibenzoylphenylethylene was isolated (12.3%) and identified by mixture melting point with an authentic sample.

A solution of phenylmagnesium bromide, made from 3 g. of magnesium, was treated with 4.75 g. of dibenzoylphenylethylene (added slowly), and the mixture poured into a cooled absolute ether solution of iodine; as the iodine color faded, more was added so that an excess was maintained (except momentarily during the addition). On hydrolysis, washing out the iodine, and working up the product, 2.1 g. (38%) of nearly pure tetraphenylfuran was isolated and identified (m. p.  $174^\circ$ ).

## Summary

Reduction of di-(trimethylbenzoyl)-ethylene by zinc and acetic acid or by catalytic hydrogen in certain solvents at  $0^\circ$  has been shown to be largely 1,6 by the formation of the moderately persistent dienol which is readily oxidizable back to the unsaturated 1,4-diketone.

Unsaturated dimesityl 1,4-diketones are prepared in a new way by hydrolysis under oxidizing conditions of the dimagnesium dienolates made from the saturated 1,4-diketone directly or from the unsaturated 1,4-diketone by reaction with an arylmagnesium halide.

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