

acetic acid in pale yellow needles, m.p. 281° (Found: C, 53.2; H, 3.1; N, 15.4), and none of the expected 7-fluoroisatin.

(b) Condensation of 2,4-difluoroaniline with chloral hydrate and hydroxylamine afforded 2,4-difluoroisatinacetamide, crystallizing from acetic acid in colorless needles, m.p. 135°.

Anal. Calcd. for C<sub>8</sub>H<sub>6</sub>F<sub>2</sub>N<sub>2</sub>O<sub>2</sub>: C, 48.0; H, 3.0; N, 14.0. Found: C, 47.7; H, 3.1; N, 14.3.

Sulfuric acid converted this anilide into a product crystal-

lizing from acetic acid in yellow prisms, m.p. 291° (dec.) (Found: C, 47.4; H, 2.5; N, 13.8.)

*Acknowledgment.* The authors express their gratitude to Dr. G. C. Finger (State Geological Survey, Urbana, Ill.,) for the gift of 2,4- and 3,4-difluoroaniline used in the present research.

PARIS VE, FRANCE

[CONTRIBUTION FROM COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA]

## Hydrogen Peroxide *cis*-Oxidative Cleavage of 2,5-Diarylfurans. Conformations and Reactions of *cis* and *trans* Methyl- and Mesityl-Dimesitylolethylenes<sup>1</sup>

ROBERT E. LUTZ AND CHI-KANG DIEN<sup>2</sup>

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Hydrogen peroxide oxidatively cleaved a series of 2,5-diarylfurans to *cis* unsaturated 1,4-diketones. In three cases 2,2'-bis-(3-furanones) were obtained as by-products stemming from  $\beta$ -oxidation.  $\beta$ -Acetoxydiphenylfuran underwent chiefly  $\alpha$ -oxidation to the 2-hydroxy-3-furanone. 2,5-Mesityl groups did not inhibit the *cis*-oxidative cleavage as in the nitric-acetic acid reactions. The mechanism of *cis*-oxidative cleavage is discussed with pertinent comments on ozonation.

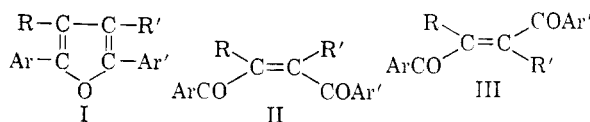
The new *cis* methyl- and mesityl-dimesitylolethylenes were shown to be labile and in this respect unlike *cis*-methylidibenzoylolethylene which is the more stable form. They underwent *cis*-acetoxy-addition-furanization. The *cis*- and *trans*-mesityl dimesitylolethylenes were reduced 1,6 to stereoisomeric di-enols which were oxidizable to the *trans* unsaturated diketone; the di-enol from the *cis* isomer furanized readily, that from the *trans* isomer did not.

The stability relationships and the differences in this respect from the phenyl analogs are explained in terms of steric consequences of the differences between the abilities of phenyl and mesityls to conjugate effectively with the unsaturated 1,4-dicarbonyl system. The different courses of the reductions of the *cis*- and *trans*-mesityl dimesitylolethylenes are explained in terms of different conformations with respect to that half of the molecule carrying the  $\alpha$ -mesityl group.

The action of hydrogen peroxide on 2,5-diarylfurans was studied for comparisons with nitric-acetic acid and lead tetraacetate oxidations,<sup>3-5</sup> and in the hope that it would bring about *cis*-oxidative cleavage of the sterically more hindered 2,5-dimesitylfurans. Such cleavage would furnish a convenient method of preparing certain *cis* unsaturated 1,4-diketones which would not be easily obtainable otherwise. The latter hope, which proved to be sound, stemmed from earlier work by Clauson-Kaas on the hydrogen peroxide oxidations of simpler furans.<sup>6,7</sup> By this reaction the new *cis*-methyl- and mesityl-dimesitylolethylenes have been obtained, completing two important *cis-trans*

pairs, and permitting a comparative study of the effect of configuration on some of the reactions of unsaturated diketone systems.

The hydrogen peroxide oxidations of the series of 2,5-diarylfurans Ia-q utilized a glacial acetic acid-30% aqueous hydrogen peroxide mixture. They are summarized in the formulations I-V and in Table I.<sup>8</sup>



- (a) Ar = Ar = C<sub>6</sub>H<sub>5</sub>, R = R' = H  
 (b) Ar = Ar = *p*-BrC<sub>6</sub>H<sub>4</sub>, R = R' = H  
 (c) Ar = Ar' = C<sub>6</sub>H<sub>5</sub>, R = Cl, R' = H  
 (d) Ar = Ar' = C<sub>6</sub>H<sub>5</sub>, R = Cl, R' = OCOCH<sub>3</sub>  
 (e) Ar = Ar' = C<sub>6</sub>H<sub>5</sub>, R = COC<sub>6</sub>H<sub>5</sub>, R' = H  
 (f) Ar = *p*-BrC<sub>6</sub>H<sub>4</sub>, Ar' = C<sub>9</sub>H<sub>11</sub> (mesityl), R = R' = H  
 (g) Ar = C<sub>6</sub>H<sub>5</sub>, Ar' = C<sub>9</sub>H<sub>11</sub>, R = H, R' = COC<sub>6</sub>H<sub>5</sub>  
 (h) Ar = Ar' = C<sub>9</sub>H<sub>11</sub>, R = R' = H  
 (i) Ar = Ar' = C<sub>9</sub>H<sub>11</sub>, R = CH<sub>3</sub>, R' = H  
 (j) Ar = Ar' = C<sub>9</sub>H<sub>11</sub>, R = R' = CH<sub>3</sub>  
 (k) Ar = Ar' = R = C<sub>9</sub>H<sub>11</sub>, R' = H  
 (l) Ar = Ar' = C<sub>9</sub>H<sub>11</sub>, R = C<sub>6</sub>H<sub>5</sub>, R' = H  
 (m) Ar = Ar' = C<sub>9</sub>H<sub>11</sub>, R = CH<sub>3</sub>, R' = Br  
 (n) Ar = Ar' = C<sub>9</sub>H<sub>11</sub>, R = R' = Br  
 (o) Ar = Ar' = C<sub>9</sub>H<sub>11</sub>, R = OCOCH<sub>3</sub>, R' = H  
 (p) Ar = Ar' = C<sub>9</sub>H<sub>11</sub>, R = OCOCH<sub>3</sub>, R' = CH<sub>3</sub>  
 (q) Ar = Ar' = C<sub>9</sub>H<sub>11</sub>, R = OCOCH<sub>3</sub>, R' = C<sub>6</sub>H<sub>5</sub>

(1) This work was supported in part by a research contract with the Office of Ordnance Research, U. S. Army, and in part by a research grant from the National Science Foundation.

(2) Postdoctorate Fellow, 1953-1956. Present location, National Aniline Division, Allied Chemical and Dye Corp., Buffalo, N. Y.

(3) R. E. Lutz and F. N. Wilder, *J. Am. Chem. Soc.*, **56**, 978 (1934).

(4) R. E. Lutz and W. P. Boyer, *J. Am. Chem. Soc.*, **63**, 3189 (1941).

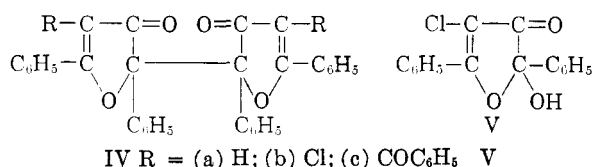
(5) C.-K. Dien and R. E. Lutz, *J. Org. Chem.*, **22**, 1355 (1957).

(6) N. Clauson-Kaas and J. Fakstorp, *Acta Chem. Scand.*, **1**, 216 (1947).

(7) A. P. Dunlap and F. N. Peters, *The Furans*, Reinhold Publishing Corp., New York, 1953, and references cited therein; see especially pp. 49-51.

(8) The work here reported was exploratory; although attention was given to yields, extensive study was not made to develop the best preparative conditions.

2,5-Diphenylfuran (Ia) gave 30% yield of the labile *cis*-dibenzoyl ethylene (IIa), 14% of the stable *trans* isomer (IIIa) and 4.5% of the 2,2'-bis-3-furanone (IVa) which was presumably formed via  $\beta$ -oxidation through the 3-hydroxyfuran. The 2,5-di(*p*-bromophenyl)furan (Ib) gave the labile *cis* unsaturated 1,4-diketone (IIb), some of the *trans* isomer (IIIb), and a considerable amount of *p*-bromobenzoic acid resulting from breakdown of the chain. 3-Chloro-2,5-diphenylfuran (Ic) gave only the *cis* form of the corresponding unsaturated diketone plus a small yield of the (new) 2,2'-bis(3-furanone) IVb. 3-Acetoxy-4-chloro-2,5-diphenylfuran (Id), where dimolecular oxidation was minimized by the protection offered by the acetyl group, was oxidized in only small part to the bisfuranone IVb, and gave as the chief product the 2-hydroxy-3-furanone V, the result of  $\alpha$ -attack at the highly activated 2-position.



In the hydrogen peroxide oxidation of the two furans Ia and b the small yields of the stable *trans* unsaturated diketones were shown to be the result of stereoisomerization of the first-formed and very labile *cis* isomers by further experiments in the Ia series. Pure *cis* isomer IIa underwent slow rearrangement to *trans* (IIIa) under the same oxidative conditions; and oxidation of Ia under more drastic conditions gave only the *trans* product IIIa in a much larger yield. Thus oxidative cleavage consistently gives primary products of configuration corresponding to and stemming from that of the ring.

The oxidation of 3-benzoyl-2,5-diphenylfuran (Ie)<sup>9</sup> in which the nucleus should be appreciably deactivated, was successful but was significantly slower than those above.

2-Bromophenyl-5-mesitylfuran (If),<sup>4</sup> one of the two 2,5-diarylfurans in which one of the aryl groups is a mesityl, gave the *cis* unsaturated diketone and some bromobenzoic acid. 2-Mesityl-5-phenyl-3-benzoylfuran (Ig)<sup>10</sup> reacted also but gave only a very small yield of the *cis* unsaturated diketone IIIg, which must result from configurational rearrangement of the as yet unknown and presumably exceptionally labile *trans* form IIg (see discussion in ref. 10).

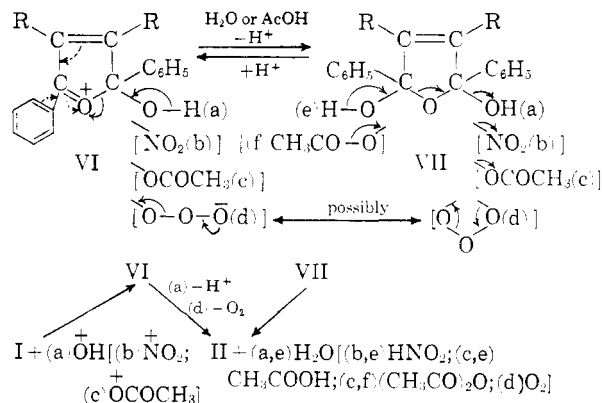
In the case of four 2,5-dimesitylfurans (Ih-k), as had been hoped, successful *cis*-oxidative cleavages occurred. 2,5-Dimesitylfuran itself (Ih) gave 40% of the very labile *cis*-dimesityloethylene (IIh)

and 20% of the *trans* isomer IIIh, whereas the other three (Ii-k) involving the  $\beta$ -substituents methyl, dimethyl and mesityl, respectively, gave only the labile *cis* products of which two are new. In four cases, Ik-n, including the 3-mesityl compound Ik, the reactions proved to be more difficult; in fact, the 3,4-dibromo compound (In) did not react significantly under the conditions employed. Unfortunately, however, of these four, only the 3-mesityl derivative Ik gave a crystalline product, the *cis* unsaturated diketone IIk.

From these results it is evident that hydrogen peroxide is a broadly applicable reagent for *cis*-oxidative cleavage of 2,5-diarylfurans and that the type of steric hindrance offered by 2,5-dimesityl groups is not as serious as it appears to be in the analogous nitric-acetic acid and lead tetraacetate reactions.<sup>4,5</sup> The hydrogen peroxide reagent shows far less tendency to attack at an open  $\beta$ -carbon than does lead tetraacetate.

**Mechanism of *cis*-oxidative cleavage.** The fact that nitric-acetic acid oxidatively cleaved a furan carrying one  $\alpha$ -mesityl group but did not attack a furan carrying two,<sup>4</sup> suggested that at least one  $\alpha$ -position must be free from excessive steric hindrance for initiation of this reaction. However, the possibility of a second step completing a 2,5-addition is not precluded by these experiments because neither the steric nor the electronic effects of either the second  $\alpha$ -position or the second entering group are the same as the first.<sup>6</sup> The successful hydrogen peroxide oxidations of 2,5-dimesitylfurans show that the steric hindrance involved is insufficient to prevent initiation of  $\alpha$ -attack by this reagent.

Assuming primary electrophilic  $\alpha$ -attack<sup>11</sup> by hydrogen peroxide, two transitory intermediates may be pictured: the cross-conjugated resonance-stabilized cation VIa ( $\sigma$ -complex) and the 2,5-(or less likely 2,3-) adduct VIIa.<sup>12</sup> The cation VIa, which is similar to that postulated in *cis*-addition furanization,<sup>10</sup> can lose a proton and give the un-



(9) C.-K. Dien and R. E. Lutz, *J. Am. Chem. Soc.*, **78**, 1987 (1956).

(10) C.-K. Dien and R. E. Lutz, *J. Org. Chem.*, **21**, 1942 (1956).

(11) Cf., L. S. Levitt, *J. Org. Chem.*, **20**, 1297 (1955).

(12) M. G. Reese, doctoral dissertation, University of Virginia, May, 1957 (two papers by R. E. Lutz and M. G. Reese, *J. Am. Chem. Soc.*, in press).

saturated 1,4-diketone of necessarily-*cis* configuration, II. The 2,5-adduct VIIa,e, which would be formed reversibly from the cation VIa and which possibly is incidental to and unnecessary for the cleavage step, could undergo concerted break-up directly to the *cis* unsaturated diketone II. In the case of the nitric-acetic acid oxidation,<sup>5</sup> the cation VIb would doubtless first undergo solvent displacement by attack at the open 5-position, directly (VIb→VIa), or stepwise (VIb→VIIb,e→VIa). Lead tetraacetate oxidation<sup>5</sup> would involve the cation VIc (probably as a lead complex<sup>11,12a</sup>) and/or the 2,5-adduct VIIc,f.

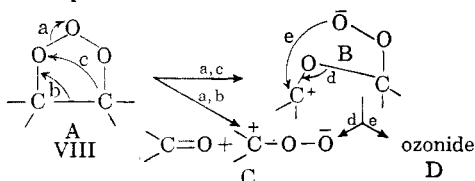
The formation of *cis*-dibenzoyl ethylene (IIa) as an ozonative *cis*-oxidation product of 2,5-diphenylfuran (Ia)<sup>13a</sup> may be interpreted similarly in terms of electrophilic attack via a resonance-stabilized ionic ( $\sigma$ -) complex<sup>14</sup> and/or 2,5-trioxy-bridged adduct<sup>13a</sup> or equilibration or hybridization between these (VIId, VIIId), in either case with subsequent release of oxygen promoted by the conjugation stabilization achieved in the end product IIa.<sup>13,15,16</sup>

(12a) Such intermediates or transitions are not unreasonable in view of the isolation of a uniquely stabilized complex seemingly of the type VI [(a) C. L. Dickerson, doctoral dissertation, University of Virginia, March, 1954], and of dialkyl analogs of the 2,5-adduct VII [(b) R. E. Lutz and M. G. Reese, *J. Am. Chem. Soc.*, paper in press].

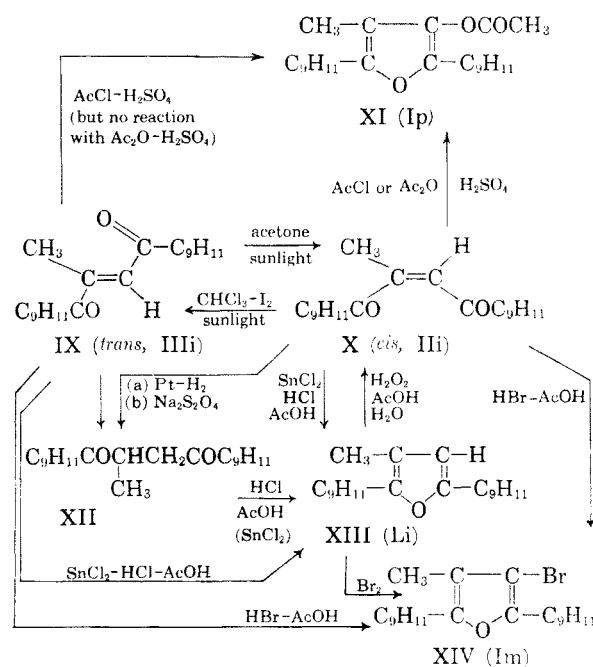
(13) (a) P. S. Bailey and H. O. Colomb, *J. Am. Chem. Soc.*, **79**, 4238 (1957). cf. also (b) The possibly analogous ozonative oxidation of anthracene [P. S. Bailey and J. B. Ashton, *J. Org. Chem.*, **22**, 98 (1957)]; (c) P. S. Bailey, *Chem. & Ind. (London)*, 1957, 1148; (d) P. S. Bailey and S. S. Bath, *J. Am. Chem. Soc.*, **79**, 3120 (1957); (e) E. A. Blair and A. Maggiolo, Abstracts, ACS Meeting, Chicago, September 7-12, 1958, p. 6P.

(14) In ozonolysis of the related methoxy- and amino-dibenzoyl ethylenes the electron-donative substituents should cause appreciable increase in resonance stabilization of a  $\sigma$ - (ionic) complex [R. E. Lutz, F. N. Wilder, and C. I. Parrish, *J. Am. Chem. Soc.*, **56**, 1980 (1934)]; in this paper the compounds formulated as VII, XV, and XVI are actually the corresponding 2-alkoxy-3-furanones].

(15) In ozonolysis mechanism<sup>15b</sup> the discarding of the molozonide ring intermediate (e.g., VIII) in favor of passage from a  $\pi$ -complex directly to a distinctly "intermediate" "zwitterion" (VIIIa) seems unsound because the geometry and resonance stabilizations necessarily involved in transitions through  $\pi$ - and/or ionic ( $\sigma$ -) complexes must involve a ring phase or transition state (e.g., VIIIa-c) which would include the postulated "zwitterion" (VIIIa) as a relatively high-energy resonance form among the several that are possible. Implicit in this view is the possibility of tautomerism between the 4- and 5-membered ring phases and the ionic complexes, and/or resonance contributions by one to the other. Break-up of the ring phase might be concerted (e.g., a,b), or stepwise [e.g., (a) and (c) followed by (d) and/or (e)]; and solvent attack (e.g., methanol<sup>15d</sup>) might occur at any of the points A-D.



*The Methylidimesitoyl ethylenes.* The availability of the new *cis* isomer X through hydrogen peroxide oxidation of the furan XIII has led to the experiments outlined below which were designed to corroborate the structures and configurations and to compare the reactivities of the *cis-trans* pair X and IX.



The furan XIII,<sup>17a</sup> although now obtained in crystalline form, was purified by distillation. The three samples made by reductive-furanizations of the *cis*- and *trans*-methylidimesitoyl-ethylenes X and IX and by dehydration of the saturated diketone XII, were identified by conversion in 95% yield or better into the same crystalline bromo derivative XIV which was prepared in another way by hydrogen-bromide addition-furanizations of the *cis* and *trans* unsaturated diketones.

The configuration of the *trans* isomer IX, based on synthesis from mesaconyl chloride and mesitylene,<sup>17a</sup> is now confirmed by the hydrogen peroxide oxidation of the furan to the new unsaturated diketone which therefore must be *cis* (X).

The *trans* isomer IX (like *trans*-dibenzoyl-ethylene) was isomerized to *cis* (X) in acetone solution under the influence of sunlight, whereas the *cis* isomer (like *cis*-dibenzoyl-ethylene) was converted also under sunlight irradiation into the *trans* isomer in chloroform solution by iodine as catalyst, or by the catalytic action of bromine without irradiation but with powdered sodium carbonate present to prevent generation and accu-

(16) The light-catalyzed autoxidation of a furan to a *cis* unsaturated diketone may also be related [G. O. Schenk, *Angew. Chem.*, **64**, 12 (1952)].

(17) (a) R. E. Lutz and D. H. Terry, *J. Am. Chem. Soc.*, **64**, 2426 (1942); (b) R. E. Lutz and R. J. Taylor, *J. Am. Chem. Soc.*, **55**, 1168 (1933).

mulation of acid. These transformations prove that the *cis* isomer, like *cis*-dibenzoyl ethylene but unlike *cis*-methyl dibenzoyl ethylene,<sup>18</sup> is the labile higher-energy form.<sup>19</sup>

The molar ultraviolet absorptivities of the *cis*- and *trans*-methyl dimesitoyl ethylenes (Fig. 1)

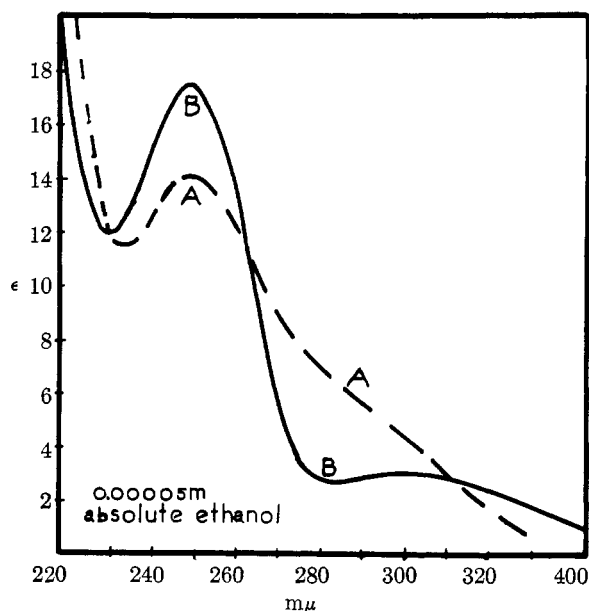


Fig. 1. Ultraviolet absorption spectra of *cis*-(A) and *trans*-(B) methyl dimesitoyl ethylenes

and the differences between them seem to be consistent with the configurations and with the steric effects postulated below. Both isomers absorb strongly at 250  $m\mu$ ; the *trans* isomer has the higher  $\epsilon$  (17,500) whereas the *cis* isomer, absorbing more broadly, has the lower  $\epsilon$  (14,000). The *trans* isomer has a broad but distinct longer wavelength band at 300  $m\mu$ ,  $\epsilon$  3,000, whereas the *cis* isomer has a corresponding longer wave-length absorptivity in the form of a shoulder on the absorption curve at *ca.* 290  $m\mu$ .

As a further check on the *cis-trans* relationship typical acetoxy-addition-furanizations were carried out. Acetyl chloride-sulfuric acid converted the *cis* isomer to the acetoxyfuran XI as it did the *trans* isomer.<sup>17a</sup> The acetic anhydride-sulfuric acid reagent, however, was stereo-selective and, as in numerous other series, converted the *cis* isomer into the acetoxyfuran under conditions which did not affect the *trans* isomer. This, therefore, constituted

(18) R. E. Lutz and P. S. Bailey, *J. Am. Chem. Soc.*, **67**, 2229 (1945).

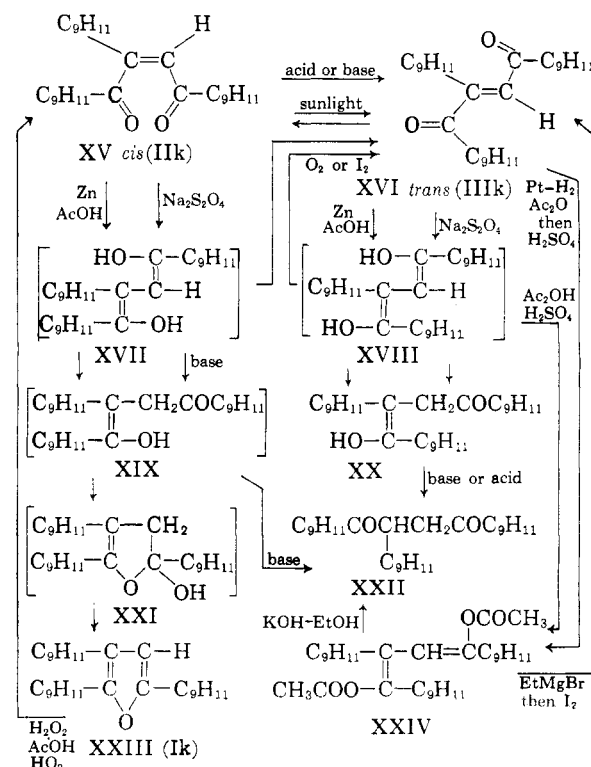
(19) At no point was evidence found of the existence of the theoretically possible methylene isomer of the type  $C_6H_5COC(=CH_2)CH_2COC_6H_5$ , which in the methyl dibenzoyl ethylene series is the stable form and the one to which the others rearrange.<sup>20</sup>

(20) *Cf.*, P. S. Bailey, G. Nowlin, S. H. Pomerantz, J. V. Waggoner, and E. E. Kawas, *J. Am. Chem. Soc.*, **73**, 5560 (1951).

still another unequivocal case of *cis*-addition-furanization.

Several comparative reduction experiments on the *cis*- and *trans*-methyl dimesitoyl ethylenes revealed no significant differences in behavior such as are found in the analogous *cis*- and *trans*-mesityl dimesitoyl ethylene pair XV and XVI. Both isomers X and IX were reduced by platinum-hydrogen or sodium hydrosulfite to the saturated diketone XII, and by stannous chloride-hydrochloric-acetic acid combination to the furan XIII (under the latter conditions the saturated diketone itself, XII, underwent dehydrative-furanization). Although these similar reduction results might be thought of as involving a common intermediate di-enol, it is quite possible, perhaps probable, that two different di-enols analogous to XVII and XVIII are produced from *cis* and *trans* conformations of the type XV and XVI, but give similar end results under the very limited variety of conditions so far employed.

*The mesityl dimesitoyl ethylenes.* The new *cis* isomer XV has been obtained only by hydrogen peroxide oxidative-cleavage of the furan XXIII. Conversion into the already known *trans* isomer XVI<sup>21</sup> by the action of acid or base shows it to be the labile form and in that sense analogous to the *cis* isomers of dibenzoyl ethylene and methyl dimesitoyl ethylene but unlike *cis*-dibenzoyl styrene and *cis*-methyl dibenzoyl ethylene. The labile *cis* isomer, however, is the one with the higher  $\epsilon$



(21) R. E. Lutz and C. J. Kibler, *J. Am. Chem. Soc.*, **62**, 360 (1940).

values for the two principal ultraviolet absorption areas. Irradiation of  $0.5^{-5}M$  ethanol solutions of the two isomers resulted in consistent shifts of the absorptivity curve to an intermediate position which indicated establishment of an approximately evenly balanced *cis-trans* photoequilibrium.

Acetoxy-addition-furanization of the *cis* isomer XV was easily effected by acetic anhydride-sulfuric acid reagent under conditions which were without effect on the *trans* isomer XVI. This, therefore, constitutes another case of *cis*-addition-furanization. The *trans* isomer could be converted into the acetoxyfuran by the more effective acetyl chloride-sulfuric acid reagent.

*Reduction experiments*, comparing the new *cis* isomer with the *trans*, were of particular interest because of earlier work in this series showing the existence of stereoisomeric metastable enols and di-enols.<sup>21</sup> Zinc-acetic acid reductions of the *cis* isomer gave trimesitylfuran XXIII in 95% yield whereas the *trans* isomer, as reported earlier, gave the crystalline mono-enol XX under the same conditions.<sup>21</sup> These results are interpreted in terms of 1,6-reductions through the two different di-enols XVII and XVIII which differ only in the configuration of the more persistent mono-enol group (cf., XIX and XX). They are to be contrasted with the comparable reductions of the *cis* and *trans* triphenyl analogs, the dibenzoylstyrenes, where it is the *trans* isomer and not the *cis* which favors reductive-furanization.<sup>22</sup> In the present series then we have a case of unequivocal *cis*-reductive-furanization with cyclization fully dependent for its success on the initial *cis* configuration of the unsaturated diketone.<sup>22,23</sup>

In the sodium hydrosulfite reductions of the *cis*- and *trans*-mesityldimesitylolethylenes the reaction mixtures quickly lost their yellow color but regained the color during work-up of the products which in both cases proved to be the same *trans* unsaturated diketone XVI. The results are interpreted in terms of the actually expected reductions to two di-enols XVII and XVIII, and their air oxidations to the same *trans* unsaturated diketone in successful competition under the work-up conditions with relatively slow ketonizations and furanization. Evidence in support of this view is as

(22) R. E. Lutz and C. R. Bauer, *J. Am. Chem. Soc.*, **73**, 3456 (1951).

(23) Another case of *cis*-reductive-furanization has been reported, where the *cis* isomer is much more reactive than the *trans*, namely, the reduction of the *cis*- and *trans*-dibenzoylstilbenes by the relatively powerful lithium aluminum hydride. However, this presumably does not involve conjugate reduction but rather primary 1,2-reductive attack at one *cis* carbonyl group with cyclization following and perhaps serving as an outlet or drive favoring the reduction.<sup>24,25</sup>

(24) R. E. Lutz, C. R. Bauer, R. G. Lutz, and J. S. Gillespie, *J. Org. Chem.*, **20**, 218 (1955).

(25) R. G. Lutz, master's thesis, University of Virginia, June 1955.

follows: When potassium hydroxide was added to the solutions of the isomers after reductions seemed to be complete, followed by continued refluxing, the saturated 1,4-diketone XXII was produced in both cases, the result obviously of the speeding up of the ketonizations of the intermediate di-enols by base catalysis (furanizations do not usually occur under basic conditions). In another reduction of the *cis* isomer benzene was added and the reaction mixture was quenched in ice. The benzene layer was separated under an atmosphere of nitrogen and was thus freed from the reducing agent and at the same time protected from air; it was then added to boiling alcoholic potassium hydroxide. This procedure gave only a small amount of the *trans* unsaturated diketone and a 75% yield of the saturated diketone.

Platinum-catalyzed hydrogenations at atmospheric pressure of the *cis*- and *trans*-mesityldimesitylolethylenes revealed a striking difference in facility as well as course of reduction; e.g., in comparable experiments in ethanol the *trans* isomer was reduced about sixteen times as fast as the *cis* isomer. The primary reduction products were shown to be di-enols by their oxidizability to the same *trans* unsaturated diketone; and they were shown to be different di-enols (XVII and XVIII) by the different end products isolated under various conditions of work-up. These experiments are summarized in Table III.

In the hydrogenations in ethanol the di-enol XVIII formed from the *trans* isomer was demonstrated by its ready air or iodine oxidizability back to the *trans* unsaturated diketone. The di-enol XVII from the *cis* isomer ketonized much more readily under the same conditions and gave a considerable amount of the saturated diketone XXIII; however, its presence was shown by the iodine oxidation which produced a considerable amount (50%) of the *trans* unsaturated diketone. Both di-enols under hydrogen were ketonized rapidly by piperidine to the saturated diketone XXII. Under treatment with hydrochloric acid, however, they reacted differently; the di-enol XVII from the *cis* isomer furanized whereas that from the *trans* isomer XVIII ketonized to the saturated diketone XXII.

The hydrogenations in glacial acetic acid were equally striking. Evidently partial-ketonization to XIX of the di-enol XVII produced from the *cis* isomer, and the subsequent furanization, occurred rapidly in this solvent; the furan was obtained under all conditions of work-up as in zinc-acetic acid reduction, even when iodine was added. On the other hand the di-enol XVIII from the *trans* compound was remarkably persistent in this solvent (20 hr. or more). Its presence and distinction from XVII was shown by its ready oxidation back to the *trans* unsaturated diketone by air or iodine, by its ready ketonization by hydrochloric acid to the saturated

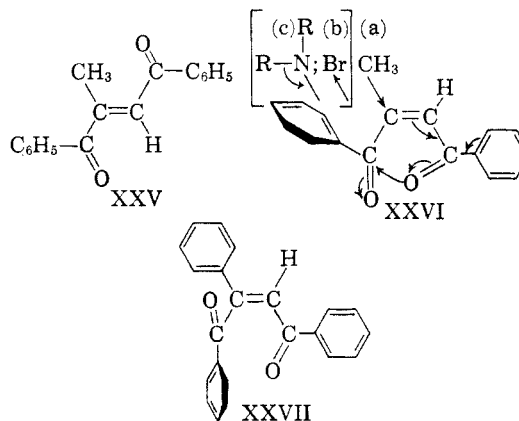
diketone, and by the fact that in no case did it ever give the furan, XXIII.

The highly persistent di-enol XVIII which has been isolated in unstable crystalline form,<sup>21</sup> has now been obtained as a stable crystalline diacetate XXIV through acetic anhydride-sulfuric acid acylation of the crude product of catalytic reduction of the *trans* (but not of the *cis*) isomer, and by catalytic reduction (of XVI) in acetic anhydride, followed by addition of a trace of concentrated sulfuric acid. This diacetate was readily hydrolyzed by alcoholic potassium hydroxide to the saturated diketone XXII and was converted by cleavage with ethylmagnesium bromide followed by oxidation with iodine, into the unsaturated diketone XVI.

*Interpretation of results.* Two striking contrasts have appeared. The relative stabilities of the *trans*- as compared with the *cis*-methyl- and mesityl-dimesitylolethylenes (IX-X, XVI-XV), are in contrast to the greater stability of *cis*- as compared with *trans*-methyl-dibenzoylethylene (XXVIa-XXV)<sup>18,26</sup>; and the reductive furanization of *cis*- but not of *trans*-mesityldimesitylolethylene (XV-XVI) is in contrast to the greater proportion of furanization in zinc-acetic acid reduction of *trans*- as compared with *cis*-dibenzoylstyrene (cf. XXVII).<sup>22</sup> These results can be explained as follows.

In the methyl-dibenzoylethylenes (XXV, XXVIa) and the dibenzoylstyrenes [XXVII, IIIa(R = C<sub>6</sub>H<sub>5</sub>)] the conjugation of the phenyl groups and their drive toward coplanarity with the carbonyl groups of the unsaturated diketone core of the molecule, must diminish the independence of this core with respect to its own individual conjugation and planarity, especially so in *cis*-dibenzoylstyrene where the chalcone conformation appears to be preeminent<sup>26</sup> and to favor 1,4- over 1,6-reduction.<sup>23</sup> On the other hand, the mesityl groups in the di- and trimesityl analogs cannot be coplanar with any part of the unsaturated diketone

core, can have only a low order of conjugation with it (i.e., "inductive"), and thus cannot as seriously affect its individual conjugation and planarity as would phenyl groups.<sup>27</sup>



In the *cis*- and *trans*-methyl-dibenzoylethylenes it is postulated that the most likely of the four types of fully conjugated conformational forms is that in which both oxygens point inward as formulated (XXV, XXVIa). The lability of the *trans* isomer has been explained in terms of the rigidly-held methyl group overlap, both of the *ortho*-hydrogen of one benzoyl, and the oxygen of the other.<sup>26a</sup> The benzoyl group on the carbon carrying the methyl, of the *cis* but not of the *trans* isomer, is unique in having the greatest steric interferences with its coplanarity; and this interference must cause considerable conformational distortion in the direction of the furanoid form, as is indicated in XXVIa.<sup>18,26b</sup> Three-dimensional molecular models clearly show this, especially the close approach of the 4-carbonyl oxygen to the 1-carbonyl carbon. Consequently, there should be a small but significant resonance contribution by this furanoid form, which, although not sufficiently large to affect noticeably the ultraviolet and infrared absorptivities of the principal chromophores,<sup>26a</sup> might be enough when coupled with purely steric inter-

(26) (a) L. P. Kuhn, R. E. Lutz, and C. R. Bauer, *J. Am. Chem. Soc.*, **72**, 5058 (1950); cf. also (b) R. E. Lutz and C. E. McGinn, *J. Am. Chem. Soc.*, **64**, 2585 (1942); and ref. 18. (c) R. E. Lutz and S. M. King, *J. Org. Chem.*, **17**, 1519 (1952). (d) R. E. Lutz and F. N. Wilder, *J. Am. Chem. Soc.*, **56**, 1193 (1934); (e) J. B. Conant and R. E. Lutz, *J. Am. Chem. Soc.*, **47**, 881 (1925); (f) The evidence for the stability relationships in the halodibenzoylethylene series, although perhaps not conclusive, is strong. Both *trans* isomers in ethanol go to the *cis* isomers under sunlight irradiation<sup>26d</sup> (experimental directions for the bromo compound which were omitted from the early paper,<sup>26d</sup> parallel those for the chloro compound). Transformations from *cis* to *trans* have not been accomplished by direct catalysis; they do not occur in chloroform-iodine solution under irradiation.<sup>26e</sup> However, in each series both *racemic* and *meso* dibenzoylethylene dihalides undergo spontaneous dehydrohalogenation in boiling ethanol with formation of considerable amounts of the *trans* and presumably therefore the stable stereoisomer.<sup>26e</sup> However, spectral evidence suggests that possibly the *cis* isomer might be the stable form.<sup>26a</sup>

(27) In respect to stability of the *trans* form the methyl- and mesityl-dimesitylolethylenes (VII-VIII and XV-XVI) are related to the diarylethylenes without ethylenic substituents, to the  $\alpha$ - and  $\beta$ -monomethylaroylacrylic series,<sup>28</sup> and to the citraconic-mesaconic pairs, where the *trans* are the stable forms. Incidentally, phenyldimesitylolethylene (dimesitylstyrene)<sup>29</sup> and mesityldibenzoylethylene<sup>30</sup> which are obtained by oxidations of the di-enols of the saturated diketones, doubtless are *cis* as postulated, the first because of the stabilizing influence of the styrene system in this form, and the latter for the reasons cited for the stability of *cis*-methyl-dibenzoylethylene<sup>26</sup> and because of its ready acetoxy-addition-furanization by acetic anhydride-sulfuric acid (cf. ref. 10, p. 1495).

(28) R. E. Lutz, P. S. Bailey, C.-K. Dien, and J. W. Rinker, *J. Am. Chem. Soc.*, **75**, 5039 (1953).

(29) R. E. Lutz and C. J. Kibler, *J. Am. Chem. Soc.*, **61**, 3010 (1939).

(30) R. E. Lutz and C. J. Kibler, *J. Am. Chem. Soc.*, **61**, 3007 (1939).

ferences, to be a decisive factor in respect to *cis-trans* stability relations just as it seems to be in some of the *cis*-furanization reactions.

Consistent with the above are: the seemingly greater stability of the *cis*-aminodibenzoyl ethylene type (cf. XXVIc) as compared with the as yet unknown *trans* type,<sup>26c</sup> where the donor effect of the nitrogen would (in the *cis* form) markedly increase the resonance contribution of the furanoid form; and the seeming lability of *cis*-bromodibenzoyl ethylene (XXVIb)<sup>26d,e</sup> where the bromine atom by electron attraction would appreciably diminish the resonance contribution of the furanoid form.

In *trans*-methyldimesityl ethylene (IX), because of the non-coplanarity of the mesityl groups and the central unsaturated diketone system, a chain-methyl overlap of an ortho methyl of the adjacent mesityl nucleus cannot exist in a sense comparable to the methyl group overlap of an ortho hydrogen in *trans*-methyl dibenzoyl ethylene (XXV). Thus the unsaturated dicarbonyl core of the *trans* molecule in both the di- and trimesityl series (IX and XVI) would appear to have significantly greater independence for its own internal conjugation and closer approach to planarity than in the *cis* form. Furthermore, the steric hindrance by mesityl groups at the carbonyl carbons would tend to minimize the resonance contribution of the furanoid form. The *trans* isomers therefore should be the stable forms, as they actually are.<sup>27</sup> Furthermore, as a consequence of the higher degree of individual conjugation and planarity of the unsaturated diketone cores, both stereoisomers should be able to undergo conjugate 1,6-reduction, as is shown actually to happen in the case of the mesityldimesityl ethylene pair.

The most favorable conformation of the *cis* trimesityl compound would seem from examination of scalar models<sup>31</sup> to be that in which both carbonyl oxygens point inward as depicted in formula XV. This is consistent with the results of reduction which proceed through the di-enol of configuration XVII, followed by partial ketonization to the persistent mono-enol XIX, and cyclodehydration via XXI to the furan XXIII. The fact that the reduction of the *trans* isomer does not involve furanization shows that the resulting di-enol and the succeeding mono-enol must have the unfavorable configurations XVIII and XX and it follows that the conformation of the precursory *trans* isomer is unique with the more hindered of the carbonyl oxygens pointing outward (rather than inward) as depicted in formula XVI. This part

(31) Herschfelder and LaPine molecular models do not take into account the effect on bond distances and angles of the unknown and varied degrees of conjugation effectiveness in these sterically hindered systems. However, they serve as a probably significant approximation and illustrate, though perhaps in somewhat exaggerated form, the nature and direction of the interference effects postulated.

of the total conformation can be deduced also from scalar models<sup>26</sup> which indicate that in the more hindered aroyl group the non-coplanar mesityl does not sterically overlap the spatially adjacent  $\beta$ -hydrogen, and that the unsaturated diketone system in this arrangement possesses the greater degree of steric freedom for conjugation as well as opportunity for the mesityl groups to assume their closest possible approach to coplanarity with the parts of the conjugated system to which they are attached.

The relatively slow catalytic hydrogenation of the *cis* isomer (as compared with the rapid hydrogenation of the *trans* isomer) is understandable in terms of a relatively high steric hindrance toward reagent attack and/or lowered conjugation effectiveness and consequent increase in the energy barrier involved in the semiquinone-like transition state or intermediate. The relative difficulty of reduction of the *cis* isomer is not inconsistent with the facility of *cis*-addition-furanization by acetic anhydride-sulfuric acid because the cyclization in reduction is a separate and final step, XIX  $\rightarrow$  XXI  $\rightarrow$  XXIII, and is not a necessary part of the mechanism of the primary reaction process as it seems to be in *cis*-addition-furanization.<sup>10</sup>

The above results and interpretations are consistent with and amplify the earlier work in this field<sup>21</sup> on the metastable enols and di-enols.

#### EXPERIMENTAL<sup>32</sup>

*Hydrogen peroxide oxidation procedure.* The furans were dissolved in glacial acetic acid and treated with 30% aqueous hydrogen peroxide under the conditions specified in Table I. The acetic acid solutions after dilution with water were extracted with benzene; the extracts were washed successively with dilute aqueous sodium carbonate and with water, dried, and evaporated under a current of air. The products were usually fractionally crystallized from ethanol, and the known compounds were identified by mixture m.p. with authentic samples.

Attempted hydrogen peroxide oxidations of the 2,5-diphenyl and 2,5-dimesityl compounds Ia and k in methanol or in *t*-butyl alcohol with or without osmium tetroxide as catalyst<sup>9</sup> at temperatures ranging from room to refluxing for 1-18 hr., gave only unchanged materials (80-90%).

2,2'-Bis(4-chloro-2,5-diphenylfuranone-3) (IVb) was obtained by hydrogen peroxide oxidations of Ie and d (Table I); recrystallized from ethyl acetate and ethanol, colorless, m.p. 300-302°. Ultraviolet absorption:  $\lambda_{\max}$  253; 319 m $\mu$ ,  $\epsilon$  17,800; 26,900;  $\lambda_{\min}$  236; 275 m $\mu$ ,  $\epsilon$  11,700; 11,400.

Anal. Calcd. for C<sub>32</sub>H<sub>20</sub>Cl<sub>2</sub>O<sub>4</sub>: C, 71.25; H, 3.74. Found: C, 70.98; H, 3.79.

*Ultraviolet absorptivity of the parent 2,2'-bis(2,5-diphenylfuranone-3) (IVa):*<sup>33</sup>  $\lambda_{\max}$  247; 306 m $\mu$ ;  $\epsilon$  14,300; 24,700.

*Ultraviolet absorptivity of 2,2'-bis(4-benzoyl-2,5-diphenyl-*

(32) (a) Microanalyses were by Misses Yuen-May Lai and B. G. Williamson. (b) Ultraviolet absorptivities were determined using a Beckman DU quartz spectrophotometer at dilutions of about 0.00005M in absolute ethanol. (c) The second and third experiments of table I were performed by G. C. Helsley.

(33) This determination was made by Dr. S. M. King, doctoral dissertation, University of Virginia, 1950, p. 89.



TABLE I<sup>8</sup>  
 HYDROGEN PEROXIDE OXIDATIONS OF FURANS

Compound	G.	30% H <sub>2</sub> O <sub>2</sub> , MI.	AcOH, MI	Reaction Temp., °C.	Time, Min.	Unchanged Material, %	Products	Yields, %
Ia	2.4	1.1	30	60-70	120		IIa, IIIa	30, 14 <sup>a</sup>
Ia	1.8	2.5	30	Reflux	120		IIIa	29
IIa	2.4	1.1	30	60-70	120	57	IIIa	15
Ib <sup>1,m</sup>	2	2	30	Reflux	30		IIb, IIIb	20, 30 <sup>b</sup>
Ic <sup>n</sup>	2	1	20	Reflux	30		IIc	40 <sup>c</sup>
Id <sup>o</sup>	1	2	20	100	30		VI	59 <sup>d</sup>
Ie <sup>q</sup>	1.25	0.6	20	Reflux	15	26	IIe	38
If <sup>4</sup>	1	1	20	Reflux	10		IIIf	27 <sup>e</sup>
Ig <sup>10</sup>	0.3	0.3	8	Reflux	30		IIIg	12 <sup>f</sup>
Ih <sup>p</sup>	1	1	20	Reflux	15		IIh, IIIh	47, 20 <sup>g</sup>
Ii <sup>h</sup>	1	1	20	Reflux	10 <sup>i</sup>		IIi <sup>h</sup>	55
Ij <sup>j</sup>	0.3	0.3	10	100	30		IIj	68
Ik <sup>21</sup>	1.25	1.25	40	100	40	21	IIk <sup>b</sup>	67
Il <sup>29</sup>	0.25	0.25	10	100	30	25	Oil <sup>i</sup>	
Im <sup>36</sup>	2	2	40	100	30	52	Oil	
In <sup>r</sup>	0.9	0.9	25	Reflux	10 <sup>t</sup>	90	Oil <sup>k</sup>	
Io <sup>s</sup>	1	1	20	Reflux	15		Oil	

<sup>a</sup> In addition to IIa and IIIa 2,2'-bis(3-furanone) IVa was obtained (4.5%). <sup>b</sup> *p*-Bromobenzoic acid was also obtained (14% based on a theoretical yield of two molar equivalents). <sup>c</sup> The bisfuranone IVb (new) was obtained (6%). <sup>d</sup> The bisfuranone IVc was obtained (13%). <sup>e</sup> *p*-Bromobenzoic acid was also obtained (13.5%). <sup>f</sup> The rest of the product was oil. Under milder conditions (100°, 5 min.) only unchanged material was isolated (70%). <sup>g</sup> The *trans* compound (IIIh) was isolated only after the mother liquor had been allowed to stand at room temperature for several days; presumably it was not present as such initially. <sup>h</sup> New compounds. <sup>i</sup> Preceded by heating at 100° for 40 min. <sup>j</sup> The oil resisted crystallization efforts after its chloroform solution containing a trace of added iodine was exposed to sunlight for 3 hr. <sup>k</sup> After prolonged refluxing (1 hr.) there was obtained unchanged material (45%) and an intractable oil. <sup>l</sup> R. E. Lutz and R. J. Rowlett, Jr., *J. Am. Chem. Soc.*, **70**, 1360 (1948). <sup>m</sup> R. E. Lutz and W. M. Eisner, *J. Am. Chem. Soc.*, **56**, 2699 (1934) in which ref. 4 should read: J. Thiele and H. Tossner, *Ann.*, **214** (1899). The m.p. of a purified sample, determined by G. C. Helsley; 204.5-205.5° corr. <sup>n</sup> R. E. Lutz, *J. Am. Chem. Soc.*, **48**, 2918 (1926). <sup>o</sup> R. E. Lutz, *et al.*, *J. Am. Chem. Soc.*, **59**, 2314 (1937). <sup>p</sup> R. E. Lutz, *et al.*, *J. Am. Chem. Soc.*, **60**, 716 (1938). <sup>q</sup> R. E. Lutz and R. J. Taylor, *J. Am. Chem. Soc.*, **55**, 1593 (1933). <sup>r</sup> R. E. Lutz and C. J. Kibler, *J. Am. Chem. Soc.*, **62**, 1520 (1940). <sup>s</sup> R. E. Lutz and J. L. Wood, *J. Am. Chem. Soc.*, **60**, 229 (1938).

furanone-3) (IVe)<sup>5</sup>:  $\lambda_{\max}$  255; 302 m $\mu$ ;  $\epsilon$  24,400; 15,000;  $\lambda_{\min}$  233, 280 m $\mu$ ;  $\epsilon$  13,400; 12,900.

The ultraviolet absorptivities of the three 2,2'-bisfuranones (IVa-c above) are distinctively two-banded with maxima at ca. 247-255 and ca. 302-319 m $\mu$ , and they are consistent with the structures assigned. The first two of these compounds have very closely similar curves, with much stronger absorptivities at the longer wave-length bands which are suggestive of cinnamoyl-type absorption.<sup>34</sup> The effect of the 4,4'-chlorines is, as expected, moderately bathochromic, and increases the height of the two peaks. The effect of the 4,4'-benzoyl groups however is considerable, involving sharp enhancement of the shorter wave-length absorption and diminution of the longer wave-length band. The highly conjugated 4,4'-benzoyl groups must offer considerable steric interferences in the molecule and some cross-conjugation with the nucleus to form two weakly contributing *cis*-chalcone systems which would absorb in the 300 m $\mu$  region<sup>35</sup>; and the less intense though still considerable long wave-length absorptivity is as would be expected. The benzoyl groups should have a sizable degree of conjugative independence, and this is reflected in the very high  $\epsilon$  value of the 255 m $\mu$  band.

The methyldimesityloxyethylenes. 3-Methyl-2,5-dimesitylfuran (II) obtained in earlier attempts<sup>17a</sup> was not crystalline. A mixture<sup>21</sup> of 10 g. of the crystalline saturated diketone XII,<sup>17a</sup> 55 ml. of hydriodic acid (sp. gr. 1.5), 20 ml. of acetic anhydride, 80 ml. of conc. acetic acid, and 0.5 g. of red phosphorus, was refluxed for 24 hr., filtered, hydrolyzed in

ice water, and extracted with ether. Evaporation of the ether and distillation of the pale yellow oil at 11 mm. (b.p. 200-205°) gave 8.1 g. (85%). It slowly solidified on standing (m.p. 75-78°) but was easily soluble in most organic solvents and resisted attempts to recrystallize by the usual methods. It was purified further by fractionation and obtaining a middle cut of b.p. 168-170° (1 mm.) which was used for analysis.

Anal. Calcd. for C<sub>23</sub>H<sub>26</sub>O: C, 86.75; H, 8.23. Found: C, 86.65; H, 8.46.

 TABLE II  
 ULTRAVIOLET ABSORPTIVITIES OF A SERIES OF  
 2,5-DI-MESITYLFURANS

Compound	Substituents	$\lambda_{\max}$ , m $\mu$	$\epsilon_{\max}$ $\times 10^{-3}$	$\lambda_{\min}$ , m $\mu$	$\epsilon_{\min}$ $\times 10^{-3}$
Ii	3-Methyl	266	10.2	242.5	7.6
Ij	3,4-Dimethyl	365	10.1	242	7.8
Im	3-CH <sub>3</sub> , 4-Br	[ca. 260 <sup>a</sup>	10.2 <sup>a</sup> ]		
Ip	3-CH <sub>3</sub> , 4-OCOCH <sub>3</sub>	262	11.6	241	10.3
Io	3-OCOCH <sub>3</sub>	263	12.6	240	9.5
Ik	3-mesityl	267	16.4	249	15.7
Iq	3-mesityl, 4-OCOCH <sub>3</sub>	266	15.5	248	13.4

<sup>a</sup> This value represents the longer wave length end of a shoulder extending from about 240 to 262 m $\mu$ ,  $\epsilon$  11,200-10,000.

3-Bromo-4-methyl-2,5-dimesitylfuran (Im)<sup>36</sup> was made by the action of bromine on Ii at room temperature in carbon tetrachloride; yield 90%; m.p. 139-140° after recryst-

(34) A. L. Wilds, L. W. Beck, W. J. Close, C. Djerassi, J. A. Johnson, T. L. Johnson, and C. H. Shunk, *J. Am. Chem. Soc.*, **69**, 1985 (1947).

(35) R. E. Lutz and R. H. Jordan, *J. Am. Chem. Soc.*, **72**, 4090 (1950).



tallization from isopropyl alcohol. The reported m.p.<sup>36</sup> of 159–160° was evidently in error. Original samples<sup>36</sup> made by hydrogen bromide addition-furanization of IIIi melted at 139–140° and gave no mixture m.p. depression with the present preparation.

*Anal.* Calcd. for C<sub>23</sub>H<sub>25</sub>BrO: C, 69.6; H, 6.35. Found: C, 69.27; H, 5.94.

*cis-1,4-Dimesityl-2-methylbutenedione-1,4* (Methyl dimesitylolethylene) (III). (See Table I). The crude product was purified by chromatographing a petroleum ether–benzene solution on alumina. It was only then induced to crystallize and was recrystallized from methanol, m.p. 78–79°, (mixture m.p. with the *trans* isomer, 62–66°). Ultraviolet absorptivity:  $\lambda_{\max}$  249 m $\mu$ ,  $\epsilon$  14,000;  $\lambda_{\min}$  234 m $\mu$ ,  $\epsilon$  11,500; shoulder at 292 m $\mu$ ,  $\epsilon$  5,500; inflections at 265 and 285 m $\mu$ ,  $\epsilon$  9,800 and 6,000.

*Anal.* Calcd. for C<sub>23</sub>H<sub>26</sub>O<sub>2</sub>: C, 82.59; H, 7.84. Found: C, 82.40; H, 8.26.

An oxidation by-product was isolated from later fractions of the chromatographed solution (above) as a deep yellow oil which slowly crystallized, m.p. 122–124° (7%), identified by mixture m.p. as the triketone enol,<sup>37</sup>



Treatment of the *cis* isomer with hydrogen bromide in conc. acetic acid, as did the *trans* isomer, gave the bromofuran Im in nearly quantitative yield.

Isomerization of the *cis* to the *trans* isomer took place in nearly quantitative yield when a sample in chloroform solution containing a sufficient quantity of iodine to impart and maintain color, was exposed to sunlight for 2 hr. A similar isomerization was affected by adding bromine to a solution of the *cis* isomer in chloroform containing suspended powdered sodium carbonate and allowing the mixture to stand for 30 min.; a 32% yield of *trans* isomer was isolated, together with intractable oil.

*trans-1,4-Dimesityl-2-methylbutanedione-1,4* (Methyl dimesitylolethylene) (IIIi).<sup>17b</sup> This isomer was obtained from the saturated diketone XIV by bromination in chloroform solution at 60° (the reaction was unsuccessful at room temperature) to a noncrystalline material presumably containing a monobromo derivative, and subsequent treatment of this with ether and triethylamine at room temperature for 1 hr.; yield 48%. Ultraviolet absorptivity:  $\lambda_{\max}$  249,300 m $\mu$ ;  $\epsilon$  17,600; 3,000;  $\lambda_{\min}$  230, 282 m $\mu$ ;  $\epsilon$  11,600; 2,600. The 300 m $\mu$  peak was an extremely broad one with the curve extending through 350 m $\mu$ ,  $\epsilon$  600.

Isomerization of the *trans* to the *cis* isomer (IIIi to III) was accomplished by direct exposure of a sample to a General Electric R. E. sun lamp for 2 hr. and inducing the resulting oil to crystallize; yield 40%. Exposure of IIIi in acetone solution to sunlight for 10 days gave the *cis* isomer in 48% yield. Spectrophotometric analysis of 0.00005M solutions of the *trans* isomer after 5 min. exposure to a General Electric R. E. sun lamp at the two main points of difference in the curves for the pure stereoisomers indicated that conversion to the *cis* isomer had proceeded about half way. After exposure for 1 hr. the conversion appeared to be nearly complete but the deviation of the curve from that of the *cis* isomer indicated that some other change was occurring also.

Reductions of *cis* and *trans*-methyl dimesitylolethylenes (IIi and IIIi). (a) Samples (0.4 g.) of IIIi and IIIi and also the saturated diketone XIV were subjected to the action of refluxing mixtures of 1.5 g. of stannous chloride, 8 ml. of conc. hydrochloric acid, and 20 ml. of conc. acetic acid, for 40 min. The resulting oils were brominated each with one equivalent of bromine in chloroform solution at room temperature

for 5 min. In the case of IIIi, 0.45 g. (95%) of the bromofuran Im was obtained; m.p. and mixture m.p. with an authentic sample were 135–138°. The yields of Im from IIIi and from XII were 98 and 95%, respectively.

(b) A similar stannous chloride reduction of the *trans* isomer IIIi, but at room temperature, gave a 20% yield of the saturated diketone XII, a result comparable with that previously reported.<sup>16</sup>

(c) To a nearly refluxing 70% ethanol solution of 0.48 g. of the *cis* isomer III was added 2 g. of sodium hydrosulfite. The yellow color disappeared after several minutes. A 10% solution of potassium hydroxide (5 ml.) was added and refluxing was continued for an additional 15 min. Dilution with ice water, extraction of the product with ether, evaporation and crystallization, gave 0.24 g. of XII (60%). Under similar conditions the *trans* isomer IIIi gave XII in 70% yield.

(d) Platinum catalyzed hydrogenation of the *cis* isomer III under the conditions which have already been shown to convert the *trans* isomer IIIi into the saturated diketone XII,<sup>16</sup> also gave XII in 55% yield.

*cis-Addition-furanization.* A solution of the *cis* isomer III in 10 ml. of acetic anhydride containing one drop of conc. sulfuric acid, was allowed to stand at room temperature for 7 min., and was hydrolyzed with ice water. Filtration of the product and crystallization from ethanol gave 0.48 g. (88%) of the acetoxyfuran Ip, m.p. 86–88°, identified by mixture m.p. with an authentic sample.<sup>16</sup>

Under these same conditions the *trans* isomer IIIi did not react and was recovered.

*The Mesityldimesitylolethylenes. cis-1,2,4-Trimesityl-2-butenedione-1,4* (mesityldimesitylolethylene) (IIk, XV) (see Table I) was crystallized from ethyl acetate–ethanol mixture, m.p. 154–155.5°. (It gave a 25° mixture m.p. depression with XVI.) Ultraviolet absorptivity: shoulders at 243, 295 m $\mu$ ,  $\epsilon$  18,000, 5,400. The absorption in the longer wave length region dropped slowly through  $\epsilon$  700 at 350 m $\mu$ .

*Anal.* Calcd. for C<sub>3</sub>LH<sub>3</sub>O<sub>2</sub>: C, 84.89; H, 7.82. Found: C, 84.53; H, 7.74.

*trans-1,2,4-Trimesityl-2-butenedione-1,4* (IIIk, XVI): Ultraviolet absorptivity: prominent shoulder at 245 m $\mu$ ,  $\epsilon$  13,900. The curve falls steeply, flattening sharply at 280 m $\mu$ ,  $\epsilon$  4,000 and then falling gradually through 300 and 350 m $\mu$ ,  $\epsilon$  2,700 and 800. The *cis-trans* photoequilibrium curve obtained on exposure of 0.00005M solutions for 2 hr. to a General Electric R. E. sun lamp was intermediate, indicating a ratio of *cis* to *trans* between 1–1 and 2–1.

*cis-trans Isomerizations:* (a) A solution of the *cis* isomer (XV) in ethanolic hydrogen chloride (13 hr.) developed yellow color. Evaporation and crystallization from methanol gave *trans* isomer XVI, m.p. 138–141° (80%). (b) A solution of 0.3 g. of the *cis* isomer and 0.5 g. of potassium hydroxide in 20 ml. of ethanol was refluxed for 30 min. and diluted with water. Crystallization of the precipitate from methanol gave 0.28 g. (93%) of *trans* isomer, m.p. 140–142°. (c) Exposure of an acetone solution of *trans* isomer to sunlight for 2 days, evaporation and crystallization from methanol gave only unchanged material (86%). From ultraviolet absorption measurements evenly balanced photoequilibria were obtained when 10<sup>-5</sup>M ethanol solutions of the *cis* and *trans* isomers were exposed to sunlight for 2 hr.

*cis-Addition-furanization. 4-Acetoxy-2,3,5-Trimesitylfuran* (Iq). A mixture of 0.2 g. of *cis* isomer XV in 5 ml. of acetic anhydride and one drop of conc. sulfuric acid was heated at 50–60° for 1.5 hr. and hydrolyzed with ice water. Crystallization from ethanol gave 1.85 g. (90%); recrystallized from isopropyl alcohol, m.p. 158–159°;  $\lambda_{\max}$  266 m $\mu$ ,  $\epsilon$  15,500;  $\lambda_{\min}$  247.5 m $\mu$ ,  $\epsilon$  13,400.

*Anal.* Calcd. for C<sub>33</sub>H<sub>36</sub>O<sub>3</sub>: C, 82.47; H, 7.54. Found: C, 82.26; H, 7.66.  $\lambda_{\max}$  266 m $\mu$ ,  $\epsilon$  15,500;  $\lambda_{\min}$  247.5 m $\mu$ ,  $\epsilon$  13,400.

The *trans* isomer XVI did not react under the above conditions, even at refluxing temperature.<sup>21</sup> When acetyl chloride was used instead of acetic anhydride (room temp., 1 hr.), the acetoxyfuran (Iq) was obtained (70%).

(36) R. E. Lutz and E. McGinn, *J. Am. Chem. Soc.*, **65**, 849 (1943).

(37) R. E. Lutz and D. H. Terry, *J. Am. Chem. Soc.*, **64**, 2423 (1942).

TABLE III  
PLATINUM-CATALYZED REDUCTIONS OF *cis* AND *trans*  
MESITYLDIMESITOLETHYLENES

Conditions Applied before Work-up	Products from <i>cis</i>	Yield, %	Products <sup>a</sup> from <i>trans</i>	Yield, %
A. Reductions in ethanol				
1. Direct evaporation under an air stream	XXII	16 <sup>b</sup>	XVI	80
2. Treatment with I <sub>2</sub> , room temp., 12 hr.	{ XXII XVI	{ 20 50	{ XVI XVI	{ 90 90
3. Treatment with conc. HCl, room temp., 12 hr.	XXIII	75	XXII	12 <sup>b,c</sup>
4. Treatment with piperidine, room temp., under H <sub>2</sub> , 12 hr.	XXII	95	XXII	79
B. Reductions in conc. acetic acid				
1. Dilution with water	XXIII	25 <sup>d</sup>	XVI	68 <sup>e</sup>
2. Standing at room temp., under H <sub>2</sub> for 8–20 hr.	XXIII	68 <sup>d</sup>	XVI	76 <sup>e</sup>
3. Treatment with I <sub>2</sub> , room temp., 12 hr.	{ XVI XXIII	{ 53 <sup>f</sup> 21	{ XVI XVI	{ 80 80
4. Treatment with conc. HCl, reflux 15 min.	{ XVI XXIII	{ 26 <sup>f</sup> 43	{ XXII XXII	{ 63 63
5. Treatment with Ac <sub>2</sub> O-drop conc. H <sub>2</sub> SO <sub>4</sub> , room temp., 12 hr.	Oil	...	XXIV	58

<sup>a</sup> The products were fractionally crystallized from methanol and identified by mixture m.p. <sup>b</sup> The major product was an oil. <sup>c</sup> A small amount of unidentified by-product (m.p. 158–162°) was obtained. <sup>d</sup> In these two runs, 20% and 15% yields, respectively, of XV, were obtained, obviously the result of incomplete reduction. <sup>e</sup> The product of first crystallization was nearly colorless (m.p. 80–91°) but on further crystallization the yellow color developed and the product was XVI. <sup>f</sup> Part of this yield presumably stems from rearrangement of unreduced XV.

These are preliminary experiments but they proved sufficient to demonstrate the difference in behavior of the *cis* and *trans* isomers.

*Reductions of the cis and trans isomers (XV and XVI).*

(a) A mixture of 0.2 g. of the *cis* isomer (XV), 2 g. of zinc dust, and 10 ml. of conc. acetic acid was refluxed with stirring for 40 min. and filtered. The filtrate was poured into ice water and the resulting oil was extracted with ether. Evaporation and crystallization from methanol gave 0.17 g. (90%) of furan (XXIII), m.p. 98–102°, identified by mixture m.p. The *trans* isomer XV under these conditions gave the crystalline monoenol XX (1-monoenol-A).<sup>21</sup>

(b) Refluxing for 1.5 hr. of a mixture of 0.1 g. of the *cis* isomer, 5 ml. of conc. acetic acid, 2 ml. of hydriodic acid (sp. gr. 1.5), 0.1 g. of iodine, and 0.1 g. of red phosphorus, gave the furan in nearly quantitative yield. The *trans* isomer and the saturated diketone XXII under these conditions also gave the furan in good yield.

(c) A solution of 0.2 g. of *cis* isomer and 0.5 g. of stannous chloride in 4 ml. of conc. hydrochloric acid and 10 ml. of conc. acetic acid was refluxed for 40 min. and diluted with ice water. Work-up in the usual way gave 0.14 g. (75%) of furan; from isopropyl alcohol, m.p. 99–101 (identified by mixture m.p.). Yields in similar conversions of the *trans* isomer and of the saturated diketone XXII were 47 and 80%, respectively.

(d) Reductions of 0.2 g. of the *cis* isomer with 2 g. of sodium hydrosulfite in 100 ml. of 70% ethanol (refluxing for 30 min.) gave only *trans* isomer in 55% yield. The original yellow color was discharged rapidly during reduction but returned during work-up. When, after 5 min., potassium hydroxide was added to the colorless refluxing solution and refluxing was continued for 1 hr. the color did not return and the saturated diketone XXII was obtained in nearly quantitative yield. In another experiment after refluxing for 10 min., 30 ml. of benzene was added and the mixture was cooled rapidly by adding 100 g. of ice; the colorless benzene layer was separated under nitrogen and added to boiling 80 ml. of 1% alcoholic potassium hydroxide; after refluxing this mixture for 30 min., 0.15 g. (75%) of the saturated diketone XXII and 0.28 g. (10%) of the *trans* isomer XVI were isolated.

The *trans* isomer XVI was recovered in 70% yield after reduction as above, but when the reduction mixture was treated with potassium hydroxide, it gave the saturated diketone (70%).

(e) Platinum-catalyzed hydrogenations at atmospheric pressure of *trans* isomer in ethanol solution (the catalyst was alkali-free<sup>38</sup>) required 30–110 min. for the absorption of one molecule; the *cis* isomer required 8–16 hr. The colorless filtered solutions were worked up after varying treatments and with the results given in Table III,A. In a similar series of experiments in which conc. acetic acid was the solvent, the reduction mixtures before removal of the catalyst were treated in the varying ways listed in Table III,B, and the catalyst was eliminated later during the work-up.

*1,2,4-Trimesitylbutane-1,3-diene-1,4-diol diacetate (XXIV).* Platinum-catalytic hydrogenation at atmospheric pressure of 0.7 g. of the *trans* isomer in 30 ml. of acetic anhydride followed by immediate treatment with a few drops of conc. sulfuric acid, standing for 12 hr., hydrolysis in ice water, filtration, and crystallization from methanol, gave 0.62 g. (71%) of XXIV; m.p. 180–181°.

*Anal.* calcd. for C<sub>35</sub>H<sub>39</sub>O<sub>4</sub>: C, 80.27; H, 7.51. Found: C, 79.97; H, 7.63. λ<sub>max</sub> 276 mμ, ε 22,700; λ<sub>min</sub> 252.5 mμ, ε 15,800.

The diacetate XXIV was also obtained by platinum-catalyzed reduction of the *trans* isomer in conc. acetic acid (see Table III,B5). The *cis* isomer under these conditions did not give a crystalline product.

*Hydrolysis of the diacetate XXIV.* (a) Refluxing alcoholic potassium hydroxide (30 min.) gave XXII in 25% yield; m.p. 140–144°. (b) The action of ethylmagnesium bromide in absolute ether (refluxing for 15 min.) and treatment with an ethanol solution of iodine (room temp., 40 min.) gave the *trans* unsaturated diketone XVI in 87% yield, m.p. 135–139°.

CHARLOTTESVILLE, VA.

(38) R. E. Lutz and W. G. Reveley, *J. Am. Chem. Soc.*, **61**, 1854 (1939).