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

Stereoisomeric Unsaturated Triaroylethylenes. Reductive-furanization and Cis-addition-furanization[1a]

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Received July 9, 1956

Part I. *Cis* and *trans* 1-*p*-bromobenzoyl-1,2-dibenzoylethylenes were prepared by oxidation of the corresponding furans. Equilibration by the action of sunlight and by sunlight-iodine catalysis showed the *trans* to be the more stable isomer. Reactions, and the preparation of related compounds including saturated triketones and furans are described. A variety of reductions were carried out but none followed a consistent stereochemical course. In one case the *cis* enol was produced; in another furans. Reductive-furanizations were caused by zinc acetic acid-acetic anhydride and by catalytic hydrogen, and the study of the possible intermediates showed that a *trans* enol must have been involved as the point at which the original *cis-trans* difference disappeared and cyclization occurred. The mechanism is discussed. Acid-catalyzed addition-furanization by acetic anhydride and by acetyl chloride took consistent *cis*-stereochemical courses, to the appropriate structurally-isomeric furans. The postulated mechanism involves primary protonation of the *cis* 1-aroyl oxygen with retention of configuration at the ethylene double bond through the point of ring closure. Hydrogen bromide caused non-stereospecific reductive-furanizations of the stereoisomers; a mechanism is suggested.

Part II. The 1-mesitoyl and 1-acetyl analogs of the unsaturated triketones were obtained each in only one of the two possible *cis-trans* forms. Studies showed these to be of the relatively very stable *cis* configuration. Two *cis*-addition-furanizations are described.It was shown that *cis*-reductive-furanization was involved to a small extent in stannous chloride reduction of the *cis*-1-mesitoyl compound. Different mechanisms for the reductive and dehydrative-furanizations involved are suggested.

Part III. The effects of structure and substituents on the ultraviolet absorptivities of the saturated and unsaturated triketones and the 2,5-diphenylfuran systems are discussed.

Different behaviors of stereoisomers in *cis* and *trans* pairs of 1,2-diaroylethylenes have been studied in earlier papers.[2] The *cis* and *trans* isomeric phenyldibenzoylethylenes[2a] and the dibenzoylstilbenes[2c] showed marked stereochemical differences in reductions. Many *cis*-1,2-diaroylethylenes underwent acid-catalyzed addition-cyclization more easily than did the corresponding *trans*-isomers.[2b] This report deals with a continuation of these studies and application to the triaroylethylenes and related compounds where the three groups are very similar[3] and where *cis-trans* isomerism is created by a difference in substitution between the two 1-benzoyl groups (*cf* Ia, IIa).

PART I. THE 1-*p*-BROMOBENZOYL-1,2-DIBENZOYLETHYLENE SERIES

Synthesis of the isomers. 3-(*p*-Bromobenzoyl)-2,5-diphenylfuran (Va), like the parent 3-benzoyl-2,5-diphenylfuran (Vf),[3a] was prepared by the Friedel-Crafts reaction between *p*-bromobenzoyl chloride and diphenylfuran. Nitric-acetic acid oxidation of the furan gave *cis*-1-(*p*-bromobenzoyl)-1,2-dibenzoylethylene (Ia). This *cis* compound was catalytically isomerized by the action of sunlight on a chloroform solution containing a trace of iodine, to a mixture of the isomers in which the *trans* isomer IIa was favored (the *cis-trans* ratio was approximately 1:2). Conversion of the *trans* isomer into an approximately 1:1 photoequilibrium mixture of the two isomers was brought about by exposure of an ether solution of the *trans* isomer to sunlight in the absence of added catalyst.

The above interconversions of the stereoisomers show that the *cis*-isomer Ia is the less stable of the pair but only by a very small margin, and that the stability difference is not nearly so great as in the *cis* and *trans* dibenzoylethylenes where the corresponding intertransformations go practically to completion. Because of the steric similarity between the 1-benzoyl and 1-bromobenzoyl groups which are responsible for the steroisomerism in the present case the stability differences between the two isomers must be due primarily to differences in conjugation effectivenesses and polarities of these two groups.

Preparation of related compounds. The corresponding saturated triketone, 1-(*p*-bromobenzoyl)-1,2-dibenzoylethane (IVa), was prepared by condensation of sodio *p*-bromodibenzoylmethane ($BrC_6H_4COCHNaCOC_6H_5$) with phenacyl bromide ($C_6H_5COCH_2Br$). It furanized under typical dehydrating conditions to a separable mixture of the isomeric furans, Va and VIa. Oxidation of the new furan, VIa, with nitric-acetic acids gave the ***trans***-triaroylethylene, IIa; thus the structures and configurations of both the furans and the unsaturated

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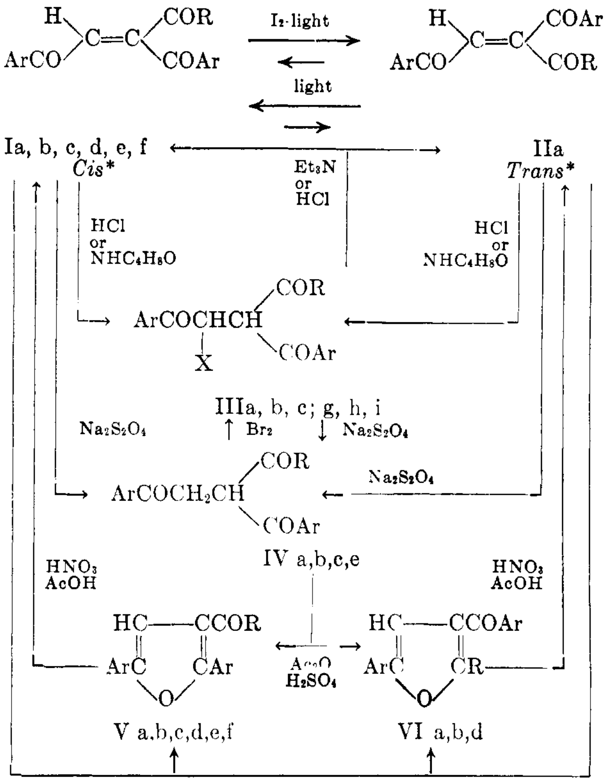
[1] (a) This work was supported in the main by a research contract between the Office of Ordnance Research, and in smaller part by a research grant from the National Science Foundation. (b) Post-doctorate Fellow. Present location, National Aniline Division, Allied Chemical and Dye Corp., Buffalo, N. Y.

[2] (a) Lutz and Bauer, *J. Am. Chem. Soc.*, **73**, 3456 (1951); (b) Lutz and Bauer, *J. Org. Chem.*, **19**, 324 (1954); (c) Lutz, Bauer, Lutz, and Gillespie, *J. Org. Chem.*, **20**, 218 (1955); (d) Kuhn, Lutz, and Bauer, *J. Am. Chem. Soc.*, **72**, 5058 (1950).

[3] (a) Dien and Lutz, *J. Am. Chem. Soc.*, **78**, 1987 (1956); (b) Lutz and Dien, *J. Org. Chem.*, **21**, 551 (1956); (c) Papers to be published shortly.

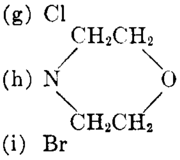


(1) $SnCl_2$-1.6 *N* HCl-86% AcOH; (2) Zn-AcOH-Ac_2O

	Ar	R
(a)	C_6H_5	$C_6H_4Br(p)$
(b)	C_6H_5	$C_6H_2(CH_3)_3$
(c)	C_6H_5	CH_3
(d)	$C_6H_4Br(p)$	CH_3
(e)	C_6H_5	$C_6H_4OCH_3(p)$
(f)	C_6H_5	C_6H_5

X

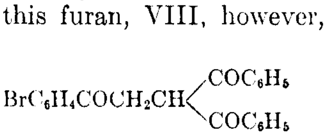
(g) Cl

(h) 

(i) Br

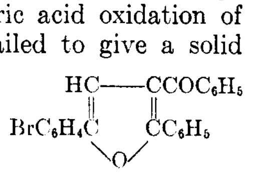
triketones were confirmed. (For discussion of ultraviolet absorption data see Part III.)

A third isomeric furan, namely, 3-benzoyl-5-(*p*-bromophenyl)-2-phenylfuran (VIII), was prepared by dehydration of 2-(*p*-bromobenzoyl)-1, 1-dibenzoylethane (VII) which had been obtained by condensation of sodio dibenzoylmethane with *p*-bromophenacyl bromide. Nitric acid oxidation of this furan, VIII, however, failed to give a solid unsaturated triketone even when the reaction was carried out at a low temperature (in propionic rather than acetic acid).



$BrC_6H_4COCH_2CH(COC_6H_5)_2$

VII



VIII

It should be noted that although the *trans* unsaturated triketone IIa could be obtained by oxidation of the furan VIa or by isomerization of the *cis*-isomer Ia, both methods involved bothersome separations of mixtures, of the furans Va and VIa, or of the *cis* and *trans*-isomers themselves (Ia and IIa).

The additions of hydrogen chloride or morpholine to both the *cis* and *trans* unsaturated triketones Ia and IIa proceeded smoothly in ether solution to give the chloro or morpholinyl saturated triketone (IIIa; g and h). The structures were assigned on the basis of analogy to earlier studies[3a] and were confirmed in the case of chloro triketone IIIa;g by dehydration to a mixture of two 4-chloro derivatives of the furans Va and VIa. It should be noted that, although diastereoisomers of the addition compounds IIIa;g and h are possible, only one and presumably the more stable form has been isolated.

Bromination of the saturated triketone IVa in carbon tetrachloride gave a bromo triketone which like the parent tribenzoyl analog was stable under acidic conditions and was assigned the structure IIIa;i by analogy.[3a] Again only one of the two possible diastereoisomers was obtained. Attempted dehydration under usual conditions failed to give the bromofuran; this represents some degree of resistance to furanization comparable to that caused by the two bromines of the dibenzoylethylene dibromides.[4] The 4-bromo-3-(*p*-bromobenzoyl)-2,5-diphenylfuran (analogous to XVIII) was subsequently obtained by bromination of the furan Va, but the isomeric furan VIa failed to react with bromine under the same conditions.

Dehydrohalogenation of the chloro and bromo saturated triketones (IIIa;g and i) as well as deamination of the morpholinyl analog IIIa;h gave mixtures of *cis* and *trans* unsaturated triketones Ia and IIa in the 1:2 catalyzed-equilibrium ratio noted above.

The chelated cis enol XII. Of the three carbonyl groups in *cis* and *trans*-1-(*p*-bromobenzoyl)-1,2-dibenzoylethylene (Ia or IIa), it would be expected that only the two which are *trans* to each other would approach a co-planar arrangement and effective through-conjugation. For the *cis* isomer this would involve the 1-*p*-bromobenzoyl and 2-benzoyl groups which are *trans* with respect to each other, (see Ia); and in this isomer the third aroyl group, like the phenyl group in *trans*-phenyldibenzoylethylene,[2a] would be non-coplanar with the long conjugated system and ineffectively conjugated with it. Conjugate (1,6) reduction[2a,c,3b,5] would be most likely to occur through the 1-bromobenzoyl and 2-benzoyl groups and should proceed stereospecifically through a dienediol which would ketonize rapidly at the less hindered end to give the specific *trans* mono enol IX; and if this *trans* mono enol were persistent enough and furanized to any extent directly as appears to happen in the phenyldibenzoylethylene series,[2a] only one

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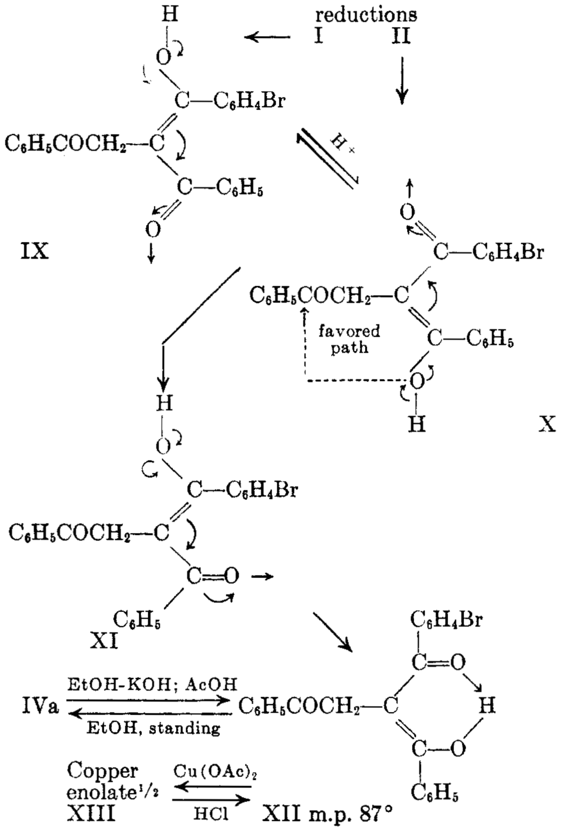
* The *cis* isomer (*cf.* I) is defined as that isomer which has the two like aroyl groups *cis* with respect to each other; and the *trans* isomer (*cf.* II) is the opposite.

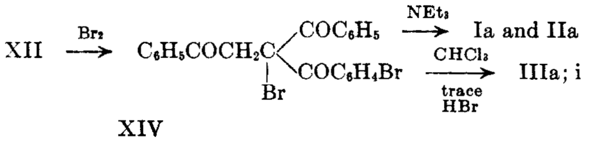
(4) Lutz, *J. Am. Chem. Soc.*, **48**, 2916 (1926).

(5) (a) Lutz, *J. Am. Chem. Soc.*, **51**, 3008 (1929); (b) Lutz and Taylor, *J. Am. Chem. Soc.*, **55**, 1993 (1933); (c) Lutz and Reveley, *J. Am. Chem. Soc.*, **61**, 1854 (1939).

of the isomeric furans would be produced thereby, namely, VIa. The *trans* unsaturated triketone IIa, if it should react likewise, would give the structurally isomeric *trans* enol X and the isomeric furan Va. Both of the *trans* enols IX and X should, like the parent tribenzoylethane analogs, be convertible to the same *cis* chelated enol XII and finally to the saturated triketone IVa.



The *trans* enols IX or/and X appear to be very fugitive. The chelated persistent *cis* enol XII, however, was obtained as an oil and in most of the experiments was handled in that form; in the end it was obtained crystalline, m.p. 85–87°. It was best produced by alcoholic-alkali enolization of the saturated triketone IVa, and it was purified by precipitation as the chloroform-soluble crystalline copper derivative XIII and regeneration by controlled acid hydrolysis under chloroform. It slowly reverted to the saturated triketone spontaneously or upon manipulations in alcohol solution. It gave a ferric chloride color test and it reacted rapidly with bromine to give an unstable crystalline 1-bromide XIV which underwent typical and rapid hydrogen bromide-catalyzed isomerization to the 2-bromide IIIa;i and dehydrohalogenation by triethylamine



$$\text{XII} \xrightarrow{Br_2} C_6H_5COCH_2\underset{\displaystyle Br}{C}\begin{cases}COC_6H_5 & \xrightarrow{NEt_3} \text{Ia and IIa} \\ COC_6H_4Br & \xrightarrow[\text{trace HBr}]{CHCl_3} \text{IIIa; i}\end{cases}$$

XIV

to the equilibrium mixture of the unsaturated triketones Ia and IIa.

Reductions of the cis and trans unsaturated triketones Ia *and* IIa. Sodium hydrosulfite reduced both stereoisomers to the saturated triketone IVa. Reductions with zinc-acetic acid-ether-water combination gave oils which in each case were shown to contain considerable amounts of *cis* enol XII (*ca.* 26%) by conversion to and isolation of the crystalline chelated copper derivative XIII. Stannous chloride reductions of the *cis* and *trans* isomers gave similar mixtures of the furans Va and VIa in ratios of 42:46 and 42:51% respectively. Samples of both the *cis* enol XII and the saturated triketone IVa in separate experiments under these same reducing conditions gave similar results.

Reductions with a zinc-acetic acid-acetic anhydride combination at 0° gave comparable mixtures of nearly equal amounts of the furans Va and VIa. However in contrast with the stannous chloride reductions, the saturated triketone IVa was shown in independent experiment to be stable under these conditions, and the *cis* enol XII underwent ketonization and not furanization. The reductive-furanization therefore cannot have involved either of these as intermediates and must have taken place through an intermediate *trans* enol or enolate in which the isomerism IX-X disappears.

In platinum-catalyzed hydrogenations in absolute ethanol of both *cis* and *trans* isomers only one compound was isolated in crystalline form, the saturated triketone IVa when minimal amounts of catalyst were used, and the furan Va when very large amounts of catalyst were used. Because the several products other than the furan Va were difficult to separate from the reaction mixtures by crystallization, aliquots were analyzed semi-quantitatively by comparison of their 250 and 300 mμ ultraviolet absorptivities with those of the known compounds. These analyses showed that in all of the experiments both saturated triketones and furans were produced in ratios depending on the proportion of catalyst used, and that large amounts of catalyst favored furanization (see Table I). The analyses did not distinguish between the furans Va and VIa, but the furan Va was the dominant and only one isolated, starting from either the *cis* or *trans* unsaturated triketones; the more soluble isomer VIa possibly was formed also but in much smaller amounts. These results are in sharp contrast with those of both stannous chloride and zinc-acetic acid-acetic anhydride reductive-furanizations where both isomeric furans were actually isolated in comparable amounts from the crude reaction products.

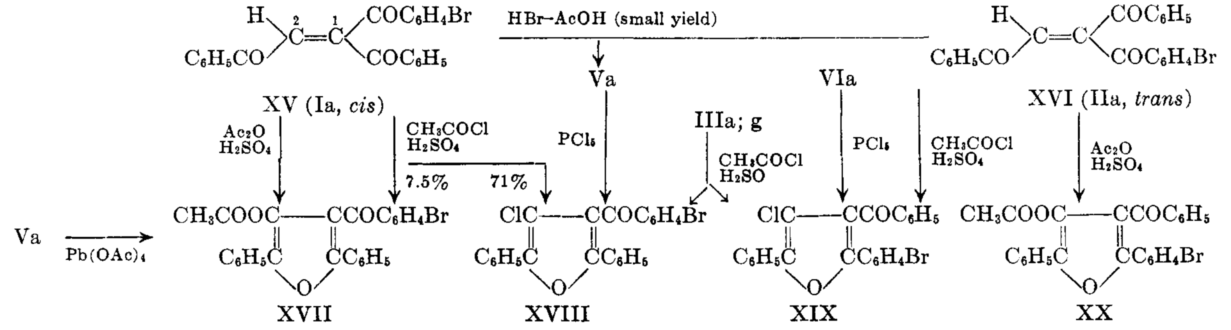
It was shown that the saturated triketone is stable under the reaction conditions once it is formed, by ultraviolet absorption analysis of the reaction mixtures at different time intervals after the up-take of hydrogen had ceased, and also by independent experiment directly upon the saturated triketone under typical reducing conditions. Also in an independent experiment, it was shown that the *cis* enol XII when subjected to the catalytic reducing conditions did not furanize but rather rearranged to the saturated triketone; and therefore the *cis* enol was not an intermediate in the furanization. It must be concluded, as in the zinc-acetic acid-acetic anhydride reduction, that the intermediate involved at the point of cyclization is a *trans* enol in which, however, isomerization-equilibration between the forms IX and X must be postulated to account for the absence of directional control of ring closure by the configuration of the starting material.

Reality and nature of the trans *enol,* IX *and/or* X. The above-described reductive-furanizations demonstrate the formation and persistence of an intermediate *trans* enol comparable to that actually isolated in the tribenzoylethylene series.[3b] The possibility of furanizations through a first formed dienediol, although not rigorously excluded, seems very unlikely because ketonization at the unhindered enolate group would be expected to be very rapid. Since the *trans* enol is able to maintain its unstable configuration, if only for a short time, one must assume in the absence of configurational control over the direction of furanization that it is not able to maintain the structural distinction represented by the two *trans* formulas IX and X [this aspect of the problem does not appear in the parent tribenzoylethylene series (If) where this type of isomerism cannot exist]. Prior *cis-trans* rearrangements in the course of the reactions, Ia ⇄IIa, are excluded as highly improbable in the light of the fact that the stereoindividualities withstand such conditions as nitric-acetic acids and the strong acids used in the *cis*-addition-furanizations described below.

The structural rearrangement between the *trans* forms IX and X may be explained in terms of acid, base, or metal surface-catalyzed isomerization-equilibration through partially resonance-stabilized anions or cations of conformation and character indicated in the composite formulations IX and X. Scalar models show this conformation to be a reasonable one and more favorable than the alternative XI in which there is considerably less freedom of motion of groups, especially of the phenacyl group. The conformations of IX and X would be stabilized by the effective conjugation of the *cis*-cinnamoyl system, and there should be a small barrier to interchange between them. The transformation to the more stable *cis* enol XII presumably would take place readily (albeit less readily than the IX-X interchange) through the unsatable and easily ionizable conformation XI with its vinyl aryl ketone conjugation.

Considering the effect of a *p*-bromine on the polarizability of the conjugated systems to which it is attached in the two alternatives IX and X, the *trans* enol form X should be the more stable of the two. That the *trans* enol does function in the sense of X rather than IX is suggested by the favored direction of furanization which on the basis of postulated mechanism would require the formulation of the intermediate as X. However this idea does not apply in the above-described zinc-acetic acid-acetic anhydride reductions where the intermediate *trans* enol is furanized to a mixture.

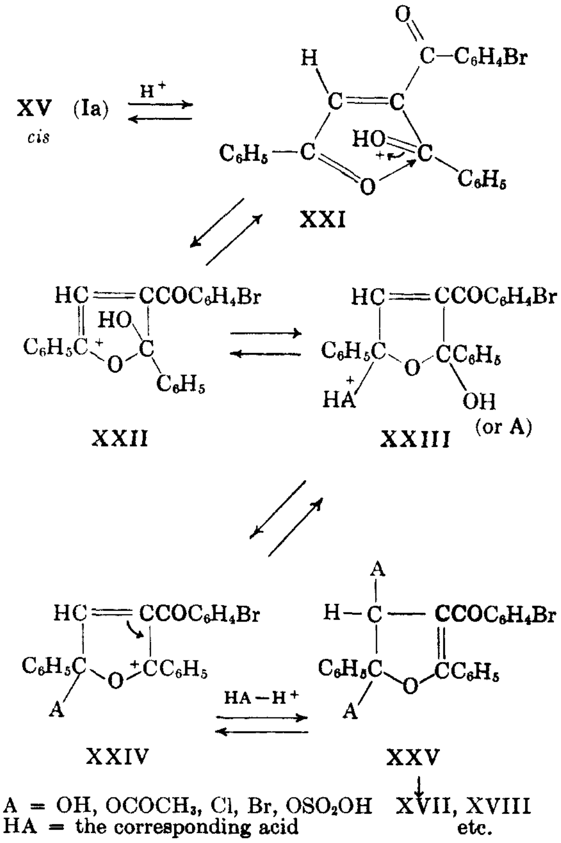
Cis-addition-furanizations. Earlier studies[2d] indicate that the addition-furanizations of certain substituted 1,2-diaroylethylenes in acidic medium involve protonated transition states which retain the original configuration, and that addition-furanization or furanone formation are thereby favored in additions to the *cis* isomers. Accordingly both of the evenly balanced *cis* and *trans* tribenzoylethylenes *para*-substituted in one of the 1-benzoyl groups, should react easily in addition-furanizations, should retain the configurations in the active transition states, and should consistently give different furans corresponding structurally to the *cis* and *trans* configurations of the starting materials. Actually, *cis*-1-(*p*-bromobenzoyl)-1,2-dibenzoylethylene, XV (Ia) was converted exclusively into 4-acetoxy-3-(*p*-bromobenzoyl)-2,5-diphenylfuran (XVII) by treatment with acetic anhydride and concentrated sulfuric acid; and treatment with acetyl chloride and sulfuric acid gave chiefly the 4-chlorofuran XVIII and a small amount of the 4-acetoxyfuran XVII. On the other hand, the *trans*-isomer, XVI (IIa), under the same conditions was converted into the structurally isomeric 4-acetoxy-3-benzoyl-2-(*p*-bromophenyl)-5-



phenylfuran (XX) and the 4-chlorofuran XIX, respectively.

Both chlorofurans (XVIII and XIX) were prepared also from their corresponding parent furans (Va and VIa) by chlorination with phosphorus pentachloride. Attempts to convert the acetoxyfurans (XVII and XX) to the corresponding chlorofurans (XVIII and XIX) by treatment with acetyl chloride-sulfuric acid or phosphorus pentachloride were not successful. The close relation between the ultraviolet absorption spectra of the acetoxyfurans (XVII and XX) and their parent furans (Va and VIa) show that the assigned structures are correct. Rigorous proof was obtained by conversion of one of the known parent furans Va by lead tetraacetate oxidation into the acetoxyfuran XVII.[3c]

From the foregoing results it is apparent that original configurations are retained in the intermediate stages during the addition-furanization up through the point of ring closure. This precludes the possibility of 1,4-addition-enolization following and directed by protonation at the *trans* 1-aroyl oxygen because the resulting addition-enolate would not likely be able to retain the original configuration of the molecule and thereby control the direction of furanization. Protonation at the 2-benzoyl oxygen and cyclization through the attack by the *cis* non-coplanar 1-aroyl oxygen *via* XXIV and XXV[2b] has been suggested to explain the *cis*-stereospecificity of the reactions. However an equally valid and perhaps more likely path is protonation at the *cis* non-coplanar 1-aroyl oxygen and reversible cyclization of configurationally stable-cations, XXI $\rightleftharpoons$ XXII with retention of both configuration and conformation of the original molecule up through the point of ring closure, followed by reactions with the reagent, XXII $\rightleftharpoons$ XXIII $\rightleftharpoons$ XXIV $\rightleftharpoons$ XXV, and by final irreversible elimination, XXV → XVII or XVIII, with generation of the resonance-stabilized furan system as the *point of no return.*



A = OH, OCOCH$_3$, Cl, Br, OSO$_2$OH
HA = the corresponding acid

Reductive-furanization by hydrogen bromide. Attempts to prepare the bromofurans analogous to XVIII and XIX by addition of dry hydrogen bromide in acetic acid to the *cis* and *trans* unsaturated triketones XV and XVI led to isolation of considerable amounts of the bromine-free furan Va (31–50%) which is at a one-stage lower oxidation level. The reaction, which is essentially a reduction, takes a course configurationally independent of the original unsaturated triketones. It does not involve the expected completed 1,4-addition product, the 1-bromide XIV or the 2-bromide IIIa;i, nor the saturated triketone IVa or its *cis* enol XII, because all of these compounds in separate experiments when subjected to these conditions reacted differently from Ia and IIa. The 2-bromide IIIa;i was stable under the reaction conditions, and the other three compounds, XIV, IVa and XII, although undergoing furanization, were furanized to quite different mixtures consisting of nearly equal amounts of the furans Va and VIa.

Analogous reductive-furanizations by hydrogen bromide have been observed;[6a] *i.e.* the conversion (in acetic acid) of di-*p*-bromobenzoyldimethylethylene into its furan,[6a] the conversion (in absolute ethanol) of *cis* and *trans*-dibenzoylbromoethylenes into 3-bromo-2,5-diphenylfuran,[6b] and the formation of the bromofuran in the bromination of tribenzoylethylene.[3a] The direction of furanization in the present case is analogous to that in catalytic hydrogenation which gave the same one of the two possible furans.

This reductive-furanization although it might be explainable in terms of a mechanism which does not involve actual addition of bromide ion at all, can most conveniently be pictured in terms of primary 1,4-addition-enolization by the relatively reactive hydrogen bromide to the *trans* addition-enolate XXVI which, because of the presence of the bromine atom, would be configurationally more stable than the *cis* enol of this series and would be particularly susceptible to furanization.[3b] The addition-enolization step is assumed to *precede* cyclization and is to be contrasted with acid-catalyzed *cis*-addition-furanization by acetyl chloride or acetic anhydride where cyclization must be assumed to come first. Reductive-elimination of

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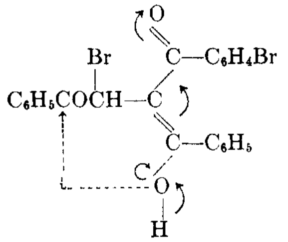
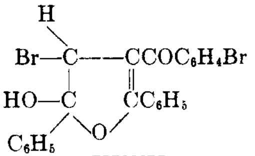
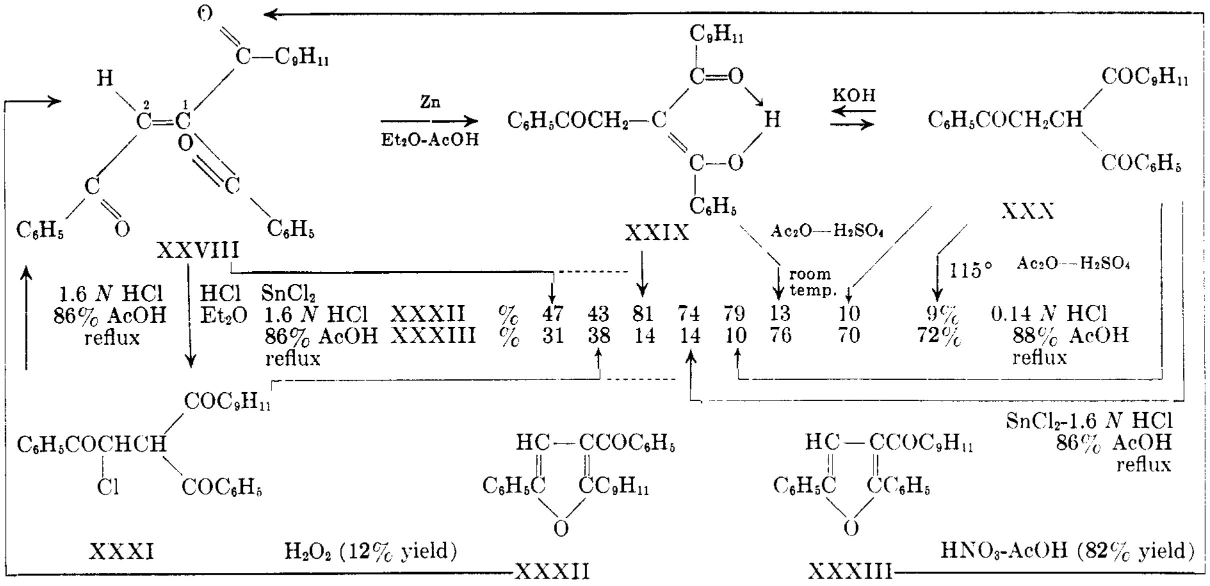
(6) (a) Couper and Lutz, *J. Org. Chem.*, **7**, 79 (1942); (b) Reese, M.S. Thesis, University of Virginia, August 1955; (c) *Cf.* also Lutz and Wilder, *J. Am. Chem. Soc*, **56**, 2065 (1934).

the "positive" bromine (or the equivalent of this) is assumed to occur either before or after cyclization (from XXVI or XXVII, to Va).


XXVI


XXVII

The debrominative (or reductive)-furanization of the 1-bromide XIV by the action of the hydrogen bromide-acetic acid reagent is to be contrasted with the "rearrangement" of the 1-bromide to the 2-bromide IIIa;i, which occurs in chloroform solution containing a very small amount of hydrogen bromide, and which has been discussed above. Dehydrohalogenation of the 1-bromide XIV to the unsaturated triketones Ia and IIa cannot have been involved here because both of these latter compounds react to give only one rather than the equi-mixture of furans Va and VIa. It must be concluded therefore that the reaction has proceeded by way of reductive-enolization (which is doubtless the first step in the "rearrangement"), through the *cis* enol XII (which would be more stable than the *trans* enol IX-X), followed by immediate furanization in the way that the *cis* enol is known to furanize under these conditions.



PART II. CIS-1-MESITOYL-1,2-DIBENZOYLETHYLENE

Cis unsaturated triketones containing a 1-acetyl or 1-mesitoyl group, Ib,c,d, in contrast with the triaroylethylenes described above, Ia, IIa, involve absent or sterically suppressed aroyl-type resonance at one of the carbonyl groups. They were prepared in good yields from the corresponding 2,5-diarylfurans by low-temperature stannic chloride-catalyzed Friedel-Crafts reactions[7] and subsequent oxidations with nitric-acetic acids. The *cis* configuration and conformation, formulated as XXVIII for the 1-mesitoyl series, are supported by the discussions to follow.

Reductions of the unsaturated triketones by sodium hydrosulfite in dilute ethanol gave the corresponding saturated triketones IVb,c,d (XXX). However in the case of one of these (Id, noncrystalline) there occurred considerable hydrolytic fission to $BrC_6H_4COCH_2CH_2COC_6H_4Br$ and BrC_6H_4COOH, which was attributed to the activating influence of the *p*-bromine. Two of the saturated triketones, IVb,d, gave the expected mixtures of furans V and VI upon dehydration.

One and the same persistent crystalline enol was obtained in the zinc reduction of mesitoyldibenzoylethylene XXVIII under non-furanizing conditions (ether-acetic acid) and by alkali-enolization of the saturated triketone XXX. This enol therefore must be the more stable of the several possible forms. It gave a normal chelated copper$_{1/2}$ derivative; and because of this, and upon steric grounds, it was assigned the *cis* configuration XXIX. This assignment was supported by examination of scalar models which showed the *cis* configuration to be by far the most favorable arrangement.

Numerous but unsuccessful efforts were made to prepare the stereoisomeric and presumably *trans* isomers of Ib and d through isomerization by absorption of light energy, under catalysis by

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[7] Lutz and Rowlett, *J. Am. Chem. Soc.*, **70**, 1359 (1948).

dine-light, acid or base, and by addition of morpholine and subsequent deamination of III-b,c;h. Oxidative cleavage of the 2-methyl and 2-mesitoyl furans (*cf.* XXXII) by nitric-acetic acid and hydrogen peroxide respectively gave only small yields of tractable products which proved to be the same as those obtained by the oxidations of the isomeric 3-acetyl and 3-mesitoyl furans (*cf.* XXXIII), and it is concluded that stereochemical rearrangement of first-formed labile unsaturated triketones to the stable forms had occurred. These results are in contrast with the stereochemically consistent nitric-acetic acid *cis*-oxidations of the isomeric furans Va and VIa to the unsaturated triketones Ia and IIa respectively, both of which are stable under the oxidation conditions.

It is evident that in the 1-acetyl and 1-mesitoyl unsaturated triketone series the known forms are the stable ones and that the as yet unknown stereoisomers are extraordinarily labile, perhaps too labile to be obtainable by ordinary preparative methods. However, the actual configurations of these compounds which have been assigned (*cf.* XXVIII) do not follow from the facts so far cited.

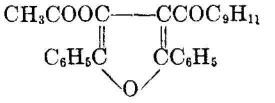
Evidence for the cis configuration. The 1-benzoyl or 1-bromobenzoyl group, in contrast with the 1-acetyl or 1-mesitoyl group, possesses effective aroyl-type conjugation in cross-conjugation with the rest of the unsaturated 1,4-diketone system of which it is a part; and the effectiveness of the cross-conjugation depends on the configuration, conformation and degree of planarity. Although the 1-acetyl or 1-mesitoyl carbonyl group should inherently be capable of more effective conjugation with the rest of the system than would the cross-conjugated carbonyl of the 1-benzoyl or 1-bromobenzoyl group, it seemed likely that steric factors would be of far greater importance in determining the relative stabilities of the stereoisomers as in the *cis* and *trans* methyl- and phenyl-dibenzoylethylene series[2a,d]

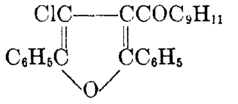
$$C_6H_5COCH{=}C(CH_3 \text{ or } C_6H_5)COC_6H_5, \quad \text{XXXIV},$$

where the *cis* isomers are the stable forms. Examination of scalar models of the 1-acetyl and 1-mesitoyl compounds Ib,c,d showed unequivocally that by far the least strained arrangement is the postulated *cis*-configuration and conformation XXVIII. In this arrangement the *cis* 1-benzoyl group (or 1-*p*-bromobenzoyl group of Id) is non-coplanar with the rest of the molecule and conjugatively independent of it, and the 1-acetyl or 1-mesitoyl carbonyl group is a part of a planar *trans*-benzoylacrylyl system in which the 2-benzoyl or 2-*p*-bromobenzoyl and the 1-acetyl or 1-mesitoyl oxygens point inward. The non-coplanar 1-benzoyl or 1-bromobenzoyl group should function as a largely independent chromophore and contribute heavily toward ultraviolet absorptivity in the 245–255 mμ region; and the through-conjugated *trans*-benzoylacrylyl system should be relatively free from steric interferences with planarity and should cause significant absorptivity in the 265–285 mμ region.

The ultraviolet absorption curves of these compounds (Fig. 2B,C) actually show the predicted high aroyl-type absorptivity and lower but pronounced longer wave length absorptivity. The curve *C* for mesitoyldibenzoylethylene is to be compared with those of *trans*-benzoylmesitoylethylene and *trans*-dibenzoylethylene (Fig. 2E,D) which contain respectively the two longer effectively conjugated systems postulated for the *cis* and *trans* forms of the unsaturated triketone. These results are consistent with and support the *cis* formulation XXVIII for Ib,c,d.

Cis-addition-furanization of *cis*-1-mesitoyl-1,2-dibenzoylethylene (XXVIII) by acetic anhydride and sulfuric acid gave the 4-acetoxyfuran XXXV the structure of which was established by a second and unequivocal synthesis directly from the furan XXXIII by lead tetraacetate oxidation.[3c] Similar *cis*-addition-furanization to XXVIII occurred with the reagent acetyl chloride-sulfuric acid to give a mixture of the corresponding acetoxy and chlorofurans XXXV and XXXVI; the structure of the latter, which was the major product, was established by synthesis from the furan XXXIII by chlorination by means of phosphorus pentachloride.


XXXV

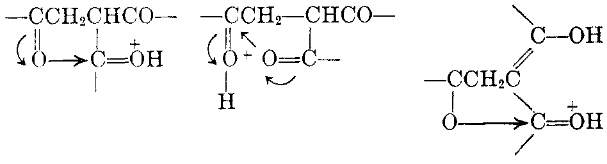

XXXVI

Reductive-furanization of *cis*-1-mesitoyl-1,2-dibenzoylethylene (XXVIII) by stannous chloride-acetic acid-conc'd hydrochloric acid combination at refluxing temperature gave a mixture of furans XXXII and XXXIII in which the former was predominant (in duplicate runs the ratios were 50:30 and 43:32 respectively). Both the saturated triketone XXX and its enol XXIX under the same reducing conditions were converted into mixtures of furans in ratios of 74:14 and 81:14 respectively, which were very similar to each other but were significantly different from that in reduction of the unsaturated triketone; and in these cases the furan XXXII was favored in still greater degrees.

The fact that the stannous chloride reduction of XXVIII gave a significantly different ratio of the two furans than that obtained from the saturated triketone XXX and its *cis* enol XXIX, is to be contrasted with reductions in the 1-bromobenzoyl-1,2-dibenzoylethylene series where no such difference appeared, and it shows that here to some extent the reduction has proceeded by a path other than through these two latter compounds. A completed 1,4-addition of hydrogen chloride giving the 2-chloro saturated triketone XXXI prior to reduction seems most unlikely because the addition compound is easily obtained and reacts with the reducing agent to give the two furans in a ratio which is the same as was obtained in reduction of the unsaturated triketone; and in independent experiments it was shown that the chloro triketone actually is quickly dehydrohalogenated to the unsaturated triketone under the conditions of reduction when the stannous chloride is omitted.

From the ratios of furans produced in the stannous chloride reductions of the unsaturated triketones it is concluded that there has occurred an increment of *cis*-reductive-furanization which could be considered as analogous to the *cis*-reductive furanizations of *cis*-dibenzoylstilbene by aluminum isopropoxide or by hydrides,[2a] but perhaps might better be expressed in terms of reduction of intermediates such as XXI-XXIII (A = Cl) formed by *cis*-addition-cyclization, in successful competition with dehydration to the chlorofuran which is stable under identical conditions once it is formed (as has been shown in independent experiment). However, without the *trans* unsaturated triketone for comparison it is not certain that the furanization is really *cis* and controlled by the configuration of the starting material.

Mechanism of dehydrative-furanization. From the above experiments it is clear that in some dehydrative-furanizations which have occurred the *trans* enol IX or X cannot be involved. This is understandable because enolizations or rearrangements of *cis* enols would not easily occur to produce the sterically strained and very transitory *trans* enols. Undoubtedly there are stereochemically less discriminate though probably less facile alternative or competing cyclization mechanisms involving protonation of one or more of the carbonyl oxygens, e.g. XXXVII-XXXIX. These mechanisms



XXXVII XXXVIII XXXIX

might well account for the striking directive dependence of the dehydrative-furanizations on conditions, which is illustrated by the almost diametrically opposite ratios of furans produced from the saturated triketone or the *cis* enol, by the acetic anhydride-sulfuric acid reagent, and by the conc'd hydrochloric-acetic acid mixture used above in the stannous chloride reductions (see Table II). The former of these two reactions was shown to be independent of the concentration of the acid, and the latter was shown to be independent of the temperature. These widely different directions of furanization pose a very interesting problem which must be related somehow to the different solvents used, acetic acid-water mixture on the one hand and acetic acid-acetic anhydride on the other, and to the difference in the two 1-carbonyl groups. However, 1-acetyl-1,2-dibromobenzoylethylene (Id) gave the same mixture of furans under the two conditions.

PART III. ULTRAVIOLET ABSORPTIVITIES

The unsaturated triketones.[cf. 2d] The absorption data for 1,1,2-tribenzoylethylene (If) (Fig. 1A) and for the *cis* and *trans* 1-(*p*-bromobenzoyl) analogs (XV and XVI) (Fig. 1B,C) are consistent with the postulated configurations and conformations. The high degree of conjugation finds reflection in large integrated absorption intensities. The parent tribenzoylethylene has its maximum at 252.5 mμ, ε 25,200, with a strong shoulder at 283 mμ, ε 15,000 (see Fig. 1A), which represents the combined effects of the two partially independent chromophores, benzoyl, and *trans* dibenzoylethylene. The *cis*-1-(*p*-bromobenzoyl) analog XV has a peak at 251 mμ and an almost equally prominent shoulder at 271 mμ (Fig. 1B); these correspond to the chromophores, benzoyl and *trans*-1-benzoyl-2-(*p*-

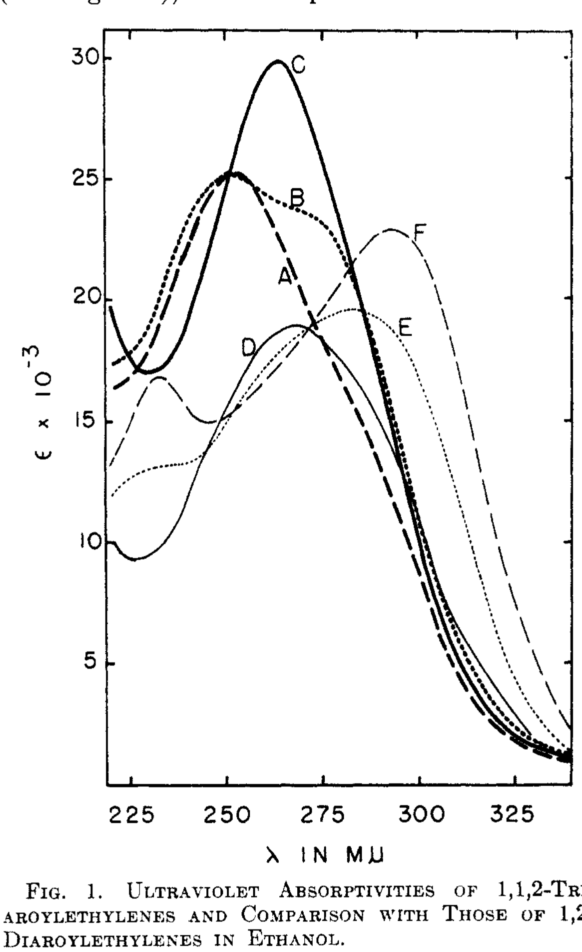


FIG. 1. ULTRAVIOLET ABSORPTIVITIES OF 1,1,2-TRIAROYLETHYLENES AND COMPARISON WITH THOSE OF 1,2-DIAROYLETHYLENES IN ETHANOL.
(A) $C_6H_5COCH{=}C(COC_6H_5)COC_6H_5$
(B) $C_6H_5COCH{=}C(COC_6H_5)COC_6H_4Br$ (*cis*)
(C) $C_6H_5COCH{=}C(COC_6H_4Br)COC_6H_5$ (*trans*)
(D) $C_6H_5COCH{=}CHCOC_6H_5$ (*trans*)
(E) $C_6H_5COCH{=}CHCOC_6H_4Br$ (*trans*)
(F) $BrC_6H_4COCH{=}CHCOC_6H_4Br$ (*trans*)

bromobenzoyl)ethylene, and involve the widest peak separation of the three compounds. The *trans*-1-(*p*-bromobenzoyl) analog XVI has a single but very strong maximum at 264 mμ (Fig. 1C), which represents contributions of two chromophores of more nearly comparable absorption wave lengths, namely *p*-bromobenzoyl and *trans*-dibenzoylethylene.

For comparison with the above, the absorptivities of the simpler *trans*-dibenzoylethylene and its mono-*p*-bromo derivative are included in Fig. 1(D,E). The effect of the *p*-bromo substitution is to produce a bathochromic shift of 15 mμ. By comparing the *trans*-dibenzoylethylene[2d] curve with those of tribenzoylethylene and its *cis*-*p*-bromo derivative XV each of which have a non-coplanar 1-benzoyl group, it is seen that in the first case (Fig. 1D) there is no shorter wave length band attributable to a benzoyl group acting as a simple or partially independent chromophore, as there are in the two latter cases (Fig. 1A,B).

Incidentally it is of interest to note that substitution of one and two *para* bromines in *trans*-dibenzoylethylene produces bathochromic effects of 15 and 23 mμ respectively (Fig. 1E, F). Also there is a sizable bathochromic effect (relative to the shoulder of curve B) upon *para*-substitution of bromine in the *trans*-1-benzoyl group of tribenzoylethylene (Fig. 1A,B). These effects are in contrast with the slight hypsochromic effect of analogous *para*-substitution of bromine in the benzoyl group of *trans* chalcone.[8]

In comparison with the above, the absorption curves of 1-acetyl and 1-mesitoyl-1,2-dibenzoylethylenes (Fig. 2B,C) are distinctive. These contain prominent benzoyl-type bands at ca. 247 mμ and prominent shoulders at *ca.* 280 mμ, ε 11,000 which must represent the *trans*-$C_6H_5COCH{=}CCOR$ system (where R = CH_3 or mesityl). Since *trans* - 1,2 - dimesitoylethylene (Fig. 2F) has only small absorptivity in the 275 mμ range (ε 1,200) as compared with *trans*-dibenzoylethylene (Fig. 2D), it was interesting to find that 1-benzoyl-2-mesitoylethylene, $C_6H_5COCH{=}CHCOC_9H_{11}$, absorbs strongly at 242 mμ, ε 15,800 and also has a shoulder at 285 mμ, ε 8,300 (Fig. 2E). The longer wave length shoulder is attributed to the long conjugated system, whereas the shorter wave length band is presumed to be due to the mesityl group affected inductively by the long conjugated system. The substitution of one and then the second mesitoyl for benzoyl in *trans*-dibenzoylethylene has produced a progressive drop in the longer wave length absorptivity peaks from ε 18,800 (at 269 mμ), to 8,300 (at *ca.* 285 mμ), and to 2,400 (at 310 mμ). The first drop is comparable to the effect of substitution of mesitoyl for the *trans*-1-benzoyl of tribenzoylethylene.

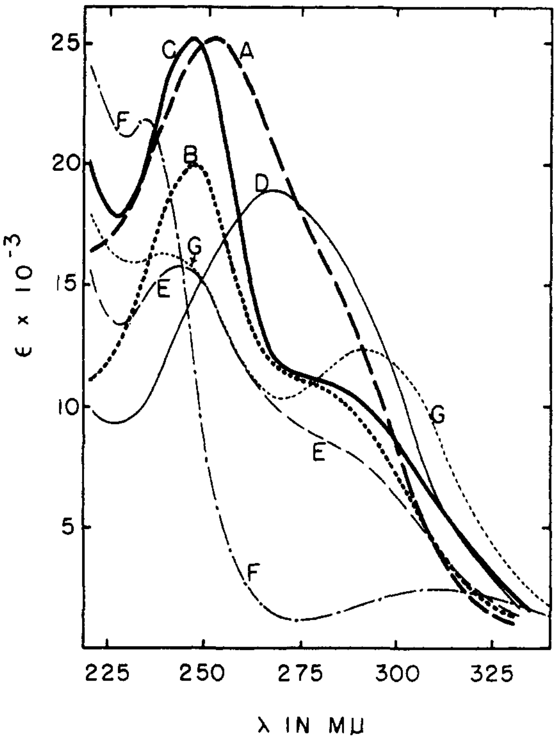


Fig. 2. Effect or Acetyl and Mesitoyl Groups on the Ultraviolet Absorptivities of Unsaturated Di- and Tri-ketones.

(A) $C_6H_5COCH{=}C(COC_6H_5)COC_6H_5$
(B) $C_6H_5COCH{=}C(COCH_3)COC_6H_5$ (*cis*)
(C) $C_6H_5COCH{=}C(COC_9H_{11})COC_6H_5$ (*cis*)
(D) $C_6H_5COCH{=}CHCOC_6H_5$ (*trans*)
(E) $C_6H_5COCH{=}CHCOC_9H_{11}$ (*trans*)
(F) $C_9H_{11}COCH{=}CHCOC_9H_{11}$ (*trans*)
(G) $BrC_6H_4COCH{=}CHCOC_9H_{11}$ (*trans*)

The *para*-substitution of bromine in these compounds produced bathochromic shifts of the characteristic bands, and the bromo series offers a comparison analogous to the above. In the case of 1 - *p* - bromobenzoyl - 2 - mesitoylethylene, $BrC_6H_4COCH{=}CHCOC_9H_{11}$, the peaks are of greater size and are quite distinctive; the 291 mμ peak (ε 12,300) corresponds to the long conjugated system, and the 240 mμ band corresponds to the mesityl group (Fig. 2G) and to the similar 242 mμ band of benzoylmesitoylethylene.

The saturated triketone and their enolates. The saturated triketones showed characteristic absorptivities representing the sum of the three completely independent chromophores, with one exception, namely the 1-bromide XIV, where the absorptivity is lower, due presumably to some slight steric interference with the planarities of the 1-aroyl groups.[cf. 3a] Only in the case of the 1-anisoyl-1,2-dibenzoylethane (IVe) were the group absorptivities sufficiently different to produce fully separated peaks, 249 and 281 mμ. Only two enols were isolated as such (from IVa and b), and both were obtained as chelated copper enolates. That metastable enols and stable enolates could generally be formed was shown by the changes in

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[8] Szmant and Basso, *J. Am. Chem. Soc.*, **74**, 4397 (1952)

ultraviolet absorptivities of 0.00005 M absolute ethanol solutions upon addition of a small excess of potassium hydroxide. Characteristic longer wave length β-hydroxy chalcone bands developed. Upon acidification the absorptivities reverted to those of the saturated triketones, rapidly in the cases of triaroyl compounds, and more slowly when the 1-acetyl or 1-mesitoyl group was involved. The slow ketonization rates in the latter two cases are consistent with conclusions already drawn that the steric interferences are greater in those cases. In Fig. 3 are given the ultraviolet absorption curves of the 1-mesitoyl-1,2-dibenzoylethane, its enolate ion, and the pure enol which absorbs at slightly lower wave length and intensity than the enolate ion.

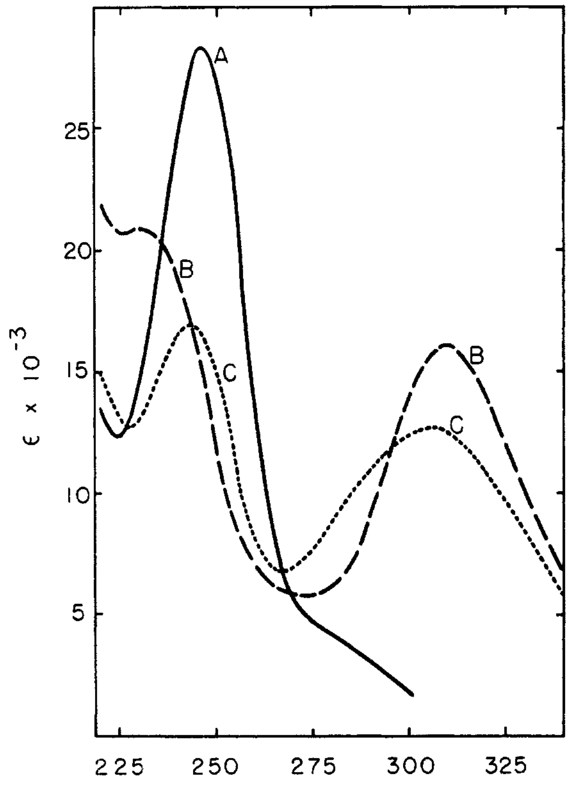
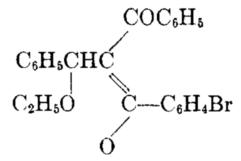
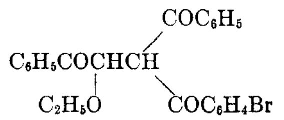


FIG. 3. ULTRAVIOLET ABSORPTIVITIY OF α-PHENACYLBENZOYLMESITOYLMETHANE AND ITS ENOL. $C_6H_5COCH_2CH(COC_6H_5)COC_9H_{11}$: (A) Keto form; (B) Enolate ion; (C) Enol.

The action of alcoholic potassium hydroxide on the 2-bromo and 2-chloro-1-p-bromobenzoyl-1,2-dibenzoylethanes (IIIa;g,i) produced typical ultraviolet absorption changes, with development of 235–240 and 335–340 mμ bands. This suggests a sequence of reactions involving dehydrohalogenation to the unsaturated triketone and addition-enolization to XL. Subsequent acidification caused deletion of the long wave length band and creation of a new absorption maximum which suggested that ketonization of XL to XLI had occurred largely, with probably some reversion to the unsaturated triketones Ia and IIa. This parallels work reported in the previous paper.[3b]



XL



XLI

The 2,5-diarylfurans. It has been observed[3a] that 3-substitution of benzoyl in 2,5-diphenylfuran (Fig. 4A,B) caused a 25 mμ hypsochromic shift of the long wave length 1,4-diphenylbutadiene band, and it was suggested that this was due to the steric interferences between the 3-benzoyl and 2-phenyl, which are readily apparent in scalar models. Smaller hypsochromic effects were noted upon similar 3-substitution of methyl, phenyl, and halogen.[9] These effects are in contrast to the bathochromic effect of 3-substitution of *tert*-amino, alkoxyl, or acetoxyl.[9] It should be noted however that the 3-benzoyl and 2-phenyl groups of Vf are parts of a *cis*-chalcone system which doubtless is also important here; it is in cross-conjugation with the 1,4-diphenylbutadiene system. The observed longer wave length band (299 mμ) lies between those of 1-phenylbutadiene (280 mμ)[10] and of 1,4-diphenylbutadiene (313–344 mμ),[11] and the shorter wave length band is at 245 mμ; these absorptivities also correspond closely to the bands of *cis*-chalcone.[12]

The still greater hypsochromic shift (34 mμ) upon β-substitution of two benzoyl groups[13] indicates still greater steric interferences. Similar but smaller hypsochromic shifts were caused by β-substitution of first one carboxyl or carbethoxyl (11 and 19 mμ, respectively) and then two carboxyls or carbethoxyls (24 and 25 mμ).[14]

If the above analysis of the effects of substitution of the 3-benzoyl group is correct (*cf.* Fig. 4A,B), it would be expected that introduction of a *para* bromine atom into the 3-benzoyl group would show little if any effect on the long wave length band since it should not directly affect the diphenylbutadiene system and would exert only a slight hypsochromic effect on the *cis*-chalcone systems; whereas the shorter wave length band, which must involve a considerable contribution by the partially independent benzoyl group of the *cis*-

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[9] King, Bauer, and Lutz, *J. Am. Chem. Soc.*, **73**, 2253 (1951).

[10] Braude, *Ann. Repts. on Prog. Chem.* (*Chem. Soc. London*), **42**, 105 (1954).

[11] Sandoval and Zachmeister, *J. Am. Chem. Soc.*, **69**, 553 (1947).

[12] (a) Lutz and Jordan, *J. Am. Chem. Soc.*, **72**, 4090 (1950); (b) Black and Lutz, *J. Am. Chem. Soc.*, **75**, 5996 (1953).

[13] Halben, *Helv. Chim. Acta*, **27**, 1265 (1944).

[14] (a) Kapf and Paal, *Ber.*, **21**, 1489 (1888); (b) Perkin and Schloesser, *J. Chem. Soc.*, **57**, 945 (1890).

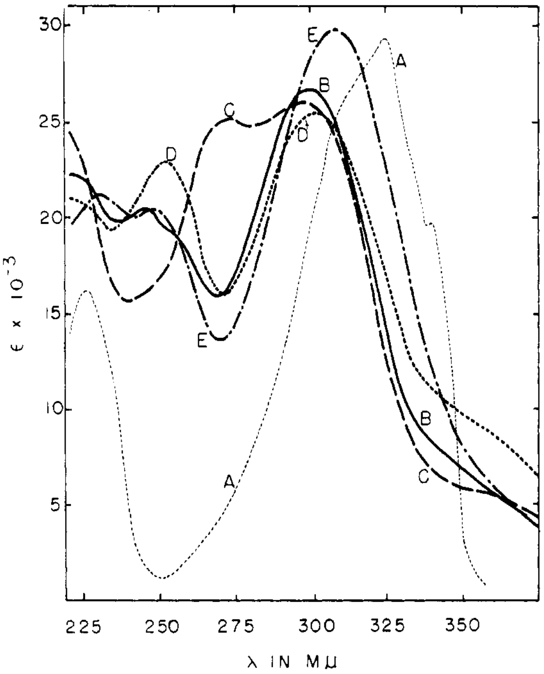

FIG. 4. EFFECT OF THE 3-AROYL GROUP ON THE ULTRAVIOLET ABSORPTIVITIES OF 2,5-DIARYLFURANS. (A) 2,5-Diphenylfuran; (B) 3-Benzoyl-2,5-diphenylfuran; (C) 3-*p*-Bromobenzoyl-2,5-diphenylfuran; (D) 3-Benzoyl-2-*p*-bromophenyl-5-phenylfuran; (E) 3-Benzoyl-2-phenyl-5-*p*-bromophenylfuran.

chalcone system, should show a marked bathochromic shift and an absorptivity corresponding to that of a partially independent *p*-bromobenzoyl group. On the other hand *para* substitution of bromine in the 2- or 5-phenyl should affect bathochromically the long wave length absorptivity of both the *cis*-chalcone and the 1,4-diphenylbutadiene systems, whereas the shorter wave length band if it is due to the benzoyl group should not be greatly affected. Actual results shown in Fig. 4C,D,E, were in agreement with these predictions. Similar effects were observed in the analogous 4-chloro and 4-acetoxy series of compounds, XVIII, XIX and XVII, XX.

It is interesting to note that in accord with expectations the 3-acetyl and 3-mesitoyl-2,5-diphenylfurans (Vb,c) as compared with the 3-benzoyl analog (Vf), (Fig. 5A,B,C), have high absorptivities at the shorter wave length band (288 mμ) which are close to that of the benzalacetone system (286 mμ),[15] and lower and shoulder-like longer wave length absorption areas in the 325-345 mμ region which correspond to contributions by the diphenylbutadiene system. 3-Acetyl-2,5-di-(*p*-bromophenyl)furan (Vd) gave an absorptivity curve (Fig. 5D) similar to that of the 2,5-diphenyl analog but with expected bathochromic shifts of both of its bands (to 303 to 335 mμ).

In this connection the effect of replacement of the 2-phenyl of 3-benzoyl-2,5-diphenylfuran by a 2-mesityl (Fig. 5E) is striking in that the long wave length band is suppressed to a mere shoulder; there is strong absorption at 282 mμ corresponding to that of a 1-phenylbutadiene system. Another related compound of interest is 2-methyl-3-(*p*-bromobenzoyl)-5-(*p*-bromophenyl)furan (Fig. 5F) where the usual 2-aryl has been replaced by methyl. Here the two principal chromophores appear to be the *p*-bromobenzoyl and *p*-bromophenylbutadiene systems which would absorb at close to the same wave length (*cf.* 283, 288 mμ).

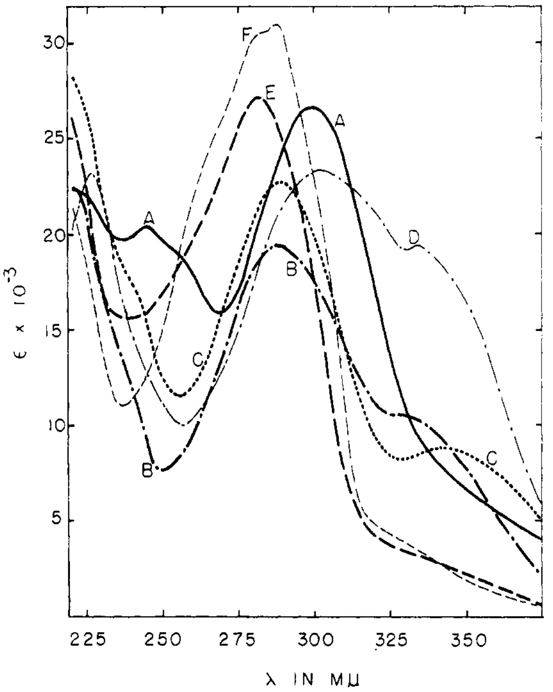

FIG. 5. ULTRAVIOLET ABSORPTIVITIES OF 3-AROYL-2,5-DIARYLFURANS IN WHICH ONE ARYL HAS BEEN REPLACED BY METHYL OR MESITYL. (A) 3-Benzoyl-2,5-diphenylfuran; (B) 3-Acetyl-2,5-diphenylfuran; (C) 3-Mesitoyl-2,5-diphenylfuran; (D) 3-Acetyl-2,5-di-*p*-bromophenylfuran; (E) 3-Benzoyl-2-mesityl-5-phenylfuran; (F) 3-*p*-Bromobenzoyl-2-methyl-5-*p*-bromophenylfuran.

EXPERIMENTAL[16]

3-(p-Bromobenzoyl)-2,5-diphenylfuran (Va). To a 110 ml. of a dry benzene solution of 16.5 g. of 2,5-diphenylfuran and 16.5 g. of crude *p*-bromobenzoyl chloride (prepared from 15 g. of *p*-bromobenzoic acid by refluxing with excess thionyl chloride and subsequently removing the excess thionyl chloride by vacuum evaporation), was added 22 g. of anhydrous stannic chloride in 30 ml. of dry benzene over a period of 20 min. The resulting dark blue mixture was stirred at 40–50° for an additional 90 min. and was hydrolyzed with ice and hydrochloric acid; a greenish-yellow precipitate (13.2 g.), and an additional 5.4 g. from the benzene layer (upon partial evaporation) was formed; yield 62%. The crude product was purified by trituration with a dilute sodium carbonate solution and repeated crystallizations from isopropyl alcohol; m.p. 158.5–159.5°

Anal. Calc'd for $C_{23}H_{15}BrO_2$: C, 68.50; H, 3.75. Found: C, 68.18; H, 3.42.

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[15] (a) Wilds, *et al.*, *J. Am. Chem. Soc.*, **69**, 1985 (1947); (b) Lutz, Bauer, and Jordan, *J. Am. Chem. Soc.*, **72**, 4300 (1950).

[16] Microanalyses were by Misses P. L. Paynter and Y. M. Lai.

1-(p-Bromobenzoyl)-1,2-dibenzoylethane (IVa). To a solution of 10 g. of sodio *p*-bromodibenzoylmethane in 150 ml. of absolute ethanol was added gradually 6.2 g. of phenacyl bromide. The mixture was refluxed for 30 min., and after acidifying with a few drops of acetic acid, it was diluted with 250 ml. of water and cooled. The resulting red-brown resin was triturated with 100 ml. of benzene. An insoluble precipitate (1:1 g.) of m.p. 210–214° was discarded. The benzene solution was evaporated under a stream of air. An ether solution of the oily residue shaken with saturated aqueous copper acetate, gave 1.3 g. of the copper enolate of unreacted *p*-bromodibenzoylmethane. Evaporation of the ether and slow crystallization of the residue from methanol gave 6.7 g. of IVa (52%) (colorless), recrystallized from methanol, m.p. 89–90°.

Anal. Calc'd for $C_{23}H_{17}BrO_3$: C, 65.57; H, 4.07. Found: C, 65.28; H, 4.26.

It gave no color test with alcoholic ferric chloride solution and showed a 20° mixture m.p. depression with *p*-bromodibenzoylmethane of m.p. 91–93°.

The *copper enolate* (XIII) was obtained through enolization of IVa, by the method described for *cis*-copper enolate of 1,1,2-tribenzoylethane;[3b] m.p. 203–205°.

Anal. Calc'd for $C_{46}H_{32}Br_2CuO_6$: C, 61.11; H, 3.57; Cu, 7.03. Found: C, 60.69; H, 3.63; Cu, 6.65.

The *enol* XII was obtained by treatment of a chloroform solution of XIII with dilute aqueous hydrochloric acid and subsequent evaporation of the chloroform solution by a stream of air. The nearly colorless enol crystallized from ether-petroleum ether mixture in 65% yield, m.p. 85–87°; mixture m.p. with IVa 75–80°.

Anal. Calc'd for $C_{23}H_{17}BrO_3$: C, 65.57; H, 4.07. Found: C, 65.75; H, 4.16.

The freshly prepared enol gave a deep red color test with alcoholic ferric chloride, and reproduced copper enolate XIII in nearly quantitative yield. Ultraviolet absorption spectral studies (see Table III) showed that the enol was very unstable in solution, even in isoöctane. For that reason, the oily enol freshly prepared from pure copper enolate was used in later experiments.

3-Benzoyl-2-(p-bromophenyl)-5-phenylfuran (VIa). Treatment of 2 g. of IVa with 20 ml. of acetic anhydride and a few drops of conc'd sulfuric acid at room temperature for 1 hour, hydrolysis with water, and elaborate fractional crystallizations of the product from isopropyl alcohol, gave 0.56 g. (29%) of the furan Va, (m.p. 155–158°, identified by mixture m.p.) and 0.39 g. (20%) of pale yellow crystals which proved to be the new isomeric furan (VIa); m.p. 114–115°.

Anal. Calc'd for $C_{23}H_{15}BrO_2$: C, 68.50; H, 3.75. Found: C, 68.56; H, 3.77.

The mixture m.p. of Va and VIa was 96–103°.

Treatment of saturated triketone IVa *and the cis enol* XII *with 20% hydrogen bromide in acetic acid* at room temperature for 45 min. gave a mixture of Va and VIa in 46, 48% and 37, 32% yields respectively; a very small amount of unidentified high-melting product (m.p. 235–245°) was also isolated in the experiment on the enol.

Treatment of IVa *and the enol* XII *with stannous chloride* under the reducing conditions used for Ia and IIa gave similar mixtures of Va and VIa, in 42, 42% and 42, 37% yields, respectively.

Treatment of IVa *with zinc-acetic acid-acetic anhydride mixture or under the conditions of the platinum-catalyzed reduction of* Ia *and* IIa, gave only unchanged IVa. The *cis* enol under these same conditions ketonized to IVa.

2-(p-Bromobenzoyl)-1,1-dibenzoylethane (VII) was prepared from 4 g. of sodio dibenzoylmethane and 4.8 g. of *p*-bromophenacyl bromide in 75 ml. of isopropyl alcohol by the method described above. The colorless product crystallized slowly from methanol, 5.35 g. (79%), m.p. 93–94°. A 15° depression of mixture m.p. with IVa was obtained.

Anal. Calc'd for $C_{23}H_{17}BrO_3$: C, 65.57; H, 4.07. Found: C, 65.41; H, 4.39.

It gave no color test with alcoholic ferric chloride and upon treatment with alcoholic sodium hydroxide (refluxing 10 min.) it was cleaved to 1-*p*-bromobenzoyl-2-benzoylethane, $C_6H_5COCH_2CH_2COC_6H_4Br$, m.p. 108–110° (identified by mixture m.p.).

A *copper enolate* was prepared[3b]; m.p. 203–204°.

Anal. Calc'd for $C_{46}H_{32}Br_2CuO_6$: Cu, 7.03. Found: Cu, 6.59.

Acidification failed to give the enol and only VII was recovered.

3-Benzoyl-2-phenyl-5-(p-bromophenyl)furan (VIII) was prepared from 1 g. of VII by the action of 10 ml. of acetic anhydride and 2 drops of conc'd sulfuric acid at room temperature (40 min.), yield 0.6 g. (63%), recrystallized from 95% ethanol; yellow; m.p. 119–119.5°.

Anal. Calc'd for $C_{23}H_{15}BrO_2$: C, 68.50; H, 3.75. Found: C, 68.48; H, 3.65.

Nitric-propionic acid *oxidation* (0°, 15 min.) gave only an oil.

cis-1-(p-Bromobenzoyl)-1,2-dibenzoylethylene (Ia). A mixture of 2 g. of the furan Va and 16 ml. of propionic acid was reacted with 2 ml. of conc'd nitric acid and was allowed to stand at 10–15° for 20 min. The red-brown solution was diluted with ice-water and the product was extracted with ether. Evaporation and crystallization of the residue from benzene-ethanol (4:6) mixture gave 1.4 g. (67%) of a pale yellow product; recrystallized, m.p. 122–123°.

Anal. Calc'd for $C_{23}H_{15}BrO_3$: C, 65.88; H, 3.61. Found: C, 66.18; H, 3.78.

trans-1-(p-Bromobenzoyl)-1,2-dibenzoylethylene (IIa) was prepared by the nitric acid oxidation of furan VIa at room temperature for 30 min.; yield 75%, recrystallized from isopropanol, m.p. 138.5–140°.

Anal. Calc'd for $C_{23}H_{15}BrO_3$: C, 65.89; H, 3.61. Found: C, 65.96; H, 3.57.

The mixture m.p. of Ia and IIa was 107–114°.

Isomerization of cis and trans-1-(p-bromobenzoyl)-1,2-dibenzoylethylene (Ia and IIa). Sunlight exposure (2 days) of a chloroform solution of the pure *cis*-isomer, containing a trace of iodine, gave a mixture (ca. 1:2) of *cis* and *trans* isomers. Exposure of an ether solution of the pure *trans*-isomer without catalyst, to sunlight for 6 hours gave approximately equal amounts of *cis* and *trans* isomers. In both cases a part of the material was resinified; the isomers were separated by fractional recrystallizations and identified by mixture m.p.

Reduction of cis and trans-1-(p-bromobenzoyl)-1,2-dibenzoylethylene (Ia and IIa). (*a*). To a solution of 2 g. of the *cis* isomer Ia in 150 ml. of 65% ethanol was added 8 g. of sodium hydrosulfite at nearly refluxing temperature. After refluxing for 30 min. and diluting with ice-water, the resulting oil was extracted with ether. Evaporation and crystallization of the product from methanol gave 1.11 g. (55%) of IVa, m.p. 89–90°. A similar reduction of *trans*-isomer IIa with sodium hydrosulfite gave IVa in 60% yield.

(*b*). One gram of *cis* isomer Ia was added to a nearly boiling solution of 2.5 g. of stannous chloride in 5 ml. of conc'd hydrochloric acid and 25 ml. of acetic acid (1.6 *N* HCl-86% AcOH). The mixture was refluxed for 10 min. and cooled. Dilution with water and fractional crystallization of the resulting precipitate from isopropyl alcohol gave 0.415 g. (43%) of furan Va (m.p. 155–158°) and 0.44 g. (46%) of furan VIa (m.p. 110–113°). Reduction of 1 g. of *trans*-isomer IIa under the same conditions gave 0.40 g. (42%) of furan Va (m.p. 154–158°) and 0.49 g. (51%) of furan VIa (m.p. 109–112°).

(*c*). One gram of zinc dust was added with stirring to a solution of 0.5 g. of Ia in 20 ml. of ether, 20 ml. of conc'd acetic acid, and 1 ml. of water, at a maintained temperature of −5 to 0°. After 20 min. the yellow mixture was filtered and diluted with water and the resulting oil was extracted with ether. Evaporation gave an orange oil which gave a deep red color test with alcoholic ferric chloride. It gradually crystallized from methanol; recrystallized, yield 0.31 g. (60%) of IVa, m.p. 88–90°, identified by mixture m.p. In a separate experiment, the above ether extract was immediately shaken with saturated aqueous copper acetate solution; copper enolate XIII (yield 24%, m.p. 203–205°) was obtained and identified by mixture m.p. *trans*-Isomer IIa under the same conditions also gave the same copper enolate XIII, yield 26%.

(*d*). Reduction of the *cis* and *trans* isomers (Ia and IIa) with zinc dust in an acetic acid and acetic anhydride (1:1) mixture at 0° for 15 min. gave a mixture of the furans Va and VIa in nearly equal amounts. Reduction with zinc-acetic acid at 50° or at refluxing temperature gave only intractable oil.

(*e*). The *cis* and *trans* isomers (Ia and IIa) were reduced catalytically at room temperature and atmospheric pressure in absolute ethanol solutions containing 0.2–0.3 g. per 100 ml. with different ratios of alkali-free[17] Adams' platinum oxide. In each experiment one equivalent of hydrogen was quickly absorbed (8–20 min.). A small aliquot was withdrawn and diluted to 0.00005 *M* for determination of ultraviolet absorptivities; and the rest of the solution was immediately filtered and worked up to isolate the products. The results with different ratios of catalyst are given in Table I. The solutions after reduction (8–20 min.) showed strong ferric chloride color tests and the absorption spectra taken immediately after dilution showed slightly lower ϵ values by *ca.* 1,000–2,000 at 252 mμ, and higher shoulders at 300 mμ, than the values which were reached after continued shaking of the reaction mixtures for an additional 30–60 min. and which are reported in Table I. It should be noted that the use of ultraviolet absorption data for analyzing is of very limited value here, and that the actual isolation of products in the specified yields constitutes sound evidence supporting the conclusion that there is a relation between the amount of catalyst and the extent of furanization.

TABLE I

PLATINUM HYDROGENATION RESULTS

Compound	Cat. ratio	λ_{max}, mμ	$\epsilon \times 10^{-3}$	% Va Calc'd[a]	Isolated[b]
Ia	0.01	252; 300[s]	34.0; 8.0	28	13[c]
Ia	0.03	252; 300[s]	26.3; 12.7	47	28
Ia	0.075	252; 301	24.2; 17.6	67	39
Ia	0.15	245;[s] 308	14.0; 15.6	59	48
IIa	0.03	252; 300[s]	25.0; 14.9	56	21
IIa	0.15	245;[s] 305	15.9; 15.4	58	38

[a] The calculated % of Va is based on the relation between the listed longer wave length λ_{max} and ϵ values and the Table III values for the saturated triketone IVa and the average of the Va and VIa values. Similar estimations of the % of IVa formed in the reaction mixtures analyzed were not made because this would call for a more complicated calculation to allow for the lower wave length absorptivities contributed by the Va and VIa present, and the loss of some of the lower wave length absorptivity due to some reduction of carbonyl groups, especially when large amounts of catalyst were used. [b] The material not accounted for was non-crystalline. [c] In this case, however, a 48% yield of the saturated triketone IVa was isolated and identified. [s] These values represent shoulders rather than distinct peaks.

4-Acetoxy-3-(p-bromobenzoyl)-2,5-diphenylfuran (XVII). (*a*). A mixture of 0.5 g. of the *cis* isomer (XV), 5 ml. of acetic anhydride, and one drop of conc'd sulfuric acid was allowed to stand at 0° for 5 min. and was hydrolyzed with ice-water. Crystallization of the resulting yellow precipitate from 80% acetic acid gave 0.48 g. of XVII (87%), m.p. 127.5–128.5°.

Anal. Calc'd for $C_{25}H_{17}BrO_4$: C, 65.09; H, 3.72. Found: C, 64.83; H, 3.87.

(*b*). A mixture of 1 g. of furan Va and 1.5 g. of lead tetraacetate in 20 ml. of acetic acid (dried by addition of 3 ml. of acetic anhydride per 100 ml.) was refluxed for 10 min. The pale yellow solution was cooled and hydrolyzed with ice-water and the product was extracted with ether. Evaporation and crystallization of the residue from methanol gave 0.35 g. (31%) of crude XVII; m.p. after recrystallization from methanol, 124–126°; identified by mixture m.p.

Treatment of XVII with acetyl chloride and conc'd sulfuric acid at room temperature for 12 hours, or at reflux temperature for 30 min., was without effect (recovery 70–80%). Treatment with phosphorus pentachloride at 100–110° for 15 min. gave only an oil.

4-Chloro-3-(p-bromobenzoyl)-2,5-diphenylfuran (XVIII). (*a*). A mixture of 1 g. of furan Va and 3 g. of phosphorus pentachloride was heated at 110–120° for 20 min. and then was hydrolyzed with ice-water. Repeated recrystallizations of the yellow product from ethanol gave 0.58 g. (53%) of XVIII, m.p. 106–107°.

Anal. Calc'd for $C_{23}H_{14}BrClO_2$: C, 63.11; H, 3.22. Found: C, 63.14; H, 3.24.

(*b*). A mixture of 0.5 g. of *cis*-isomer XV in 5 ml. of acetyl chloride was treated with one drop of conc'd sulfuric acid at 0° for 10 min. and worked up in usual way. Fractional recrystallizations from isopropyl alcohol gave 0.04 g. (7.5%) of XVII, m.p. 125–127°, and 0.37 g. (71%) of XVIII, m.p. 103–106° (identified by mixture m.p.).

1-(p-Bromobenzoyl)-2-chloro-1,2-dibenzoylethylene was prepared by nitric acid oxidation of the chlorofuran XVIII (room temperature, 20 min.) in 80% yield; recrystallized from isopropyl alcohol, m.p. 134–135°.

Anal. Calc'd for $C_{23}H_{14}BrClO_3$: C, 60.88; H, 3.11. Found: C, 60.91; H, 3.03.

The product was *reduced* by sodium hydrosulfite to IVa in 59% yield. Treatment of the product with acetic anhydride and sulfuric acid (room temperature, 20 min.) gave only an oil.

4-Acetoxy-3-benzoyl-2-(p-bromophenyl)-5-phenylfuran (XX) was prepared by the action of acetic anhydride and conc'd sulfuric acid on the *trans*-isomer XVI (0°, 7 min.). The yellow product was recrystallized from ethanol, m.p. 138–139°; yield 86%. A 30°-mixture m.p. depression with XVII was observed.

Anal. Calc'd for $C_{25}H_{17}BrO_4$: C, 65.09; H, 3.72. Found: C, 64.79; H, 3.85.

Attempts to convert XX to the corresponding chlorofuran XIX by treatment with either acetyl chloride or phosphorus pentachloride gave only intractable oils.

4-Chloro-3-benzoyl-2-(p-bromobenzyl)-5-phenylfuran (XIX) was prepared (*a*) by treatment of furan VIa with excess phosphorus pentachloride at 110–120° for 30 min. The pale yellow product crystallized from isopropyl alcohol, yield 69%, m.p. 148–149°.

Anal. Calc'd for $C_{23}H_{14}BrClO_2$: C, 63.11; H, 3.22. Found: C, 63.39; H, 3.36.

(*b*). The action of acetyl chloride and conc'd sulfuric acid on XVI at 0° for 10 min. gave 81% of XIX, m.p. 144–146°, identified by mixture m.p.

Nitric acid *oxidation* of XIX (room temperature, 25 min.) failed to give a crystalline product.

4-Bromo-3-(p-bromobenzoyl)-2,5-diphenylfuran was prepared by bromination of 2 g. of furan Va with an equivalent amount of bromine in carbon tetrachloride at nearly refluxing temperature. Evaporation of the solvent and crystallization of the resulting oil from benzene-ligroin mixture gave 2.1 g. (87%) which was repeatedly recrystallized from a methanol-benzene mixture, m.p. 100–101°.

Anal. Calc'd for $C_{23}H_{14}Br_2O_2$: C, 57.29; H, 2.93. Found: C, 57.15; H, 2.98.

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(17) Prepared by treatment of the catalyst with dilute nitric acid. *Cf.* ref. 5c.

Attempts to prepare 4-bromo-3-benzoyl-2-(p-bromophenyl)-5-phenylfuran by bromination of furan VIa under the above conditions or with a small amount of pyridine added as catalyst, failed. Only unchanged material was recovered.

Reaction of cis and trans isomers XV *and* XVI *with hydrogen bromide.* Treatment of 1 g. of *cis* isomer XV with 10 ml. of 20% hydrogen bromide in acetic acid solution (room temperature, 45 min.) gave 0.3 g. (31%) of Va; recrystallized from isopropyl alcohol, m.p. 154–156° (identified). Treatment of *trans*-isomer XVI with hydrogen bromide under the same conditions also gave only the furan Va (41%). Addition of an equivalent amount of β-naphthol[cf. 6a] during the reaction produced no notable effect. The only product isolated and identified was the furan Va (40–50%). The lower-melting and more soluble isomer VIa was probably formed in these reactions also but was not isolated.

Bromination of *cis* and *trans* isomers XV and XVI in chloroform solution (one equivalent, room temperature, 14–16 hours) gave only intractable oils.

2-Chloro-1-(p-bromobenzoyl)-1,2-dibenzoylethane (IIIa;g) was prepared from Ia by treatment with excess hydrogen chloride in 3:1 ether-benzene (room temperature, 18 hours); crystallized from ethanol, yield 64%. IIa gave the same product (70%). M.p. 166.5–168°.

Anal. Calc'd for $C_{23}H_{16}BrClO_3$: C, 60.61; H, 3.54. Found: C, 60.80; H, 3.71.

2-Bromo-1-(p-bromobenzoyl)-1,2-dibenzoylethane (IIIa;i) was prepared by bromination of IVa with an equivalent amount of bromine in carbon tetrachloride at room temperature; it was crystallized from isopropyl alcohol, yield 80%; m.p. (decomp.) 164°.

Anal. Calc'd for $C_{23}H_{16}O_3Br_2$: C, 55.23; H, 3.22. Found: C, 55.10; H, 3.70.

It was recovered unchanged after treatment with cold sodium bisulfite in dilute ethanol solution or with 20% hydrogen bromide in acetic acid (room temperature, 45 min.).

Reduction of IIIa;g *and* IIIa;i with sodium hydrosulfite in boiling 70% ethanol (30 min.) gave IVa in 40 and 60% yields, respectively.

Dehydrohalogenation of IIIa;g *and* IIIa;i with excess triethylamine in ether solution (room temperature 15–20 hours) gave Ia and IIa in *ca.* 1:2 and 1:3 ratios, respectively.

Dehydration of IIIa;g with acetyl chloride and conc'd sulfuric acid (room temperature, 1 hour) gave an 80% yield of *ca.* equal amounts of the chloro furans XVIII and XIX. Dehydration of IIIa;i with acetic anhydride and conc'd sulfuric acid was unsuccessful; at room temperature there was no reaction, and at higher temperature (100°, 1 hour) only partial change to an oil.

1-Bromo-1-(p-bromobenzoyl)-1,2-dibenzoylethane (XIV). A freshly prepared sample of enol XII (from 0.5 g. of copper enolate XIII) was treated at 0° with an equivalent amount of bromine in methanol solution; the bromine color was discharged rapidly. After diluting with ice-water, the product was extracted with chloroform. Evaporation and crystallization of the residue from a warm ethyl acetate-methanol mixture gave 0.51 g. (92%) of colorless XIV, m.p. 86–87° (turning red at the m.p.). It showed no mixture m.p. depression with IVa.

Anal. Calc'd for $C_{23}H_{16}Br_2O_3$: C, 55.23; H, 3.22. Found: C, 55.14; H, 4.03.

Dehydrohalogenation of XIV with triethylamine in ether solution gave Ia and IIa in *ca.* a 1:2 ratio.

Rearrangement of XIV to IIIa;i occurred when a 5-ml. chloroform solution containing 0.1 ml. of 20% hydrogen bromide-acetic acid was allowed to stand at room temperature for 1 hour; yield 70%.

Treatment of XIV *with 20% hydrogen bromide-acetic acid* (room temperature, 45 min.) gave Va and VIa in 45% and 25% yields, respectively.

2-Morpholinyl-1-(p-bromobenzoyl)-1,2-dibenzoylethane (IIIa;h). Addition of 2 ml. of morpholine to a solution of 1 g. of the *cis* isomer (Ia) in 50 ml. of ether caused gradual precipitation of IIIa;h. After 20 min. it was filtered and crystallized from ethanol; 1.09 g. (91%); m.p. 126–127°.

Anal. Calc'd for $C_{27}H_{24}BrNO_4$: C, 64.04; H, 4.78. Found: C, 63.35; H, 4.71.

Deamination of IIIa;h with 80% acetic acid (100°, 10 min.) gave a 1:2 mixture of Ia and IIa (identified by mixture m.p.).

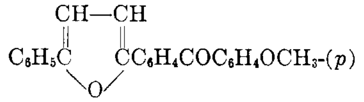
OTHER 3-AROYL-(OR ACYL)-2,5-DIARYLFURANS AND RELATED COMPOUNDS

Preparation of 3-aroyl-(or acyl)-2,5-diarylfurans by Friedel-Crafts reactions. 3-Mesitoyl-2,5-diphenylfuran (XXXIII). A mixture of 22 g. of diphenylfuran, 30 g. of stannous chloride, and 150 ml. of benzene was reacted with crude mesitoyl chloride prepared from 16.4 g. of mesitoic acid (room temperature, 1 hour, and 40–50°, 1 hour); it was recrystallized from a methanol-benzene mixture; 21 g. (58%), m.p. 128–129°.

Anal. Calc'd for $C_{26}H_{22}O_2$: C, 85.21; H, 6.05. Found: C, 85.25; H, 6.00.

3-p-Anisoyl-2,5-diphenylfuran (Ve) *and 2-(p-anisoylphenyl)-5-phenylfuran* (XLII) were prepared from 11 g. of diphenylfuran, 8.5 g. of *p*-anisoyl chloride, and 14 g. of stannous chloride in 80 ml. of benzene as above. A small amount of XLII (0.95 g., 5.4%) was obtained as an insoluble precipitate from benzene and was recrystallized from toluene; m.p. 200–201°, λ_{max} 230, 293, and 360 mμ, ε 18,700; 17,400 and 31,000, λ_{min} 260 and 312 mμ, ε 7,700 and 14,400, shoulder at 368 mμ, ε 30,100.

Anal. Calc'd for $C_{24}H_{18}O_3$: C, 81.34; H, 5.12. Found: C, 81.21; H, 5.01.



XLII

The major product Ve (15.2 g., 86%) was obtained by partial evaporation of the benzene filtrate; it was recrystallized from a benzene-ethanol mixture, m.p. 120–121°.

Anal. Calc'd for $C_{24}H_{18}O_3$: C, 81.34; H, 5.12. Found: C, 81.29; H, 4.99.

The structures were assigned to the two isomeric products Ve and XLII on the basis of the ultraviolet absorption spectra. The *p*-anisoyl compound XLII gave two peaks, one at 293 mμ and the other at *ca.* 360 mμ, and of the two structures, only XLII could account for this extraordinarily long wave length band.

3-Acetyl-2,5-diphenylfuran (Vc)[7] gave a semicarbazone (from methanol, refluxing 1 hour); recrystallized from a benzene-ethanol mixture, m.p. 215–216°.

Anal. Calc'd for $C_{19}H_{17}N_3O_2$: C, 71.45; H, 5.37. Found: C, 71.59; H, 5.23.

3-Acetyl-2,5-di(p-bromophenyl)furan (Vd)[7] was prepared like Ic but using benzene as the solvent; it was recrystallized from isopropyl alcohol, m.p. 134–135° (L. and R. 129–130°).[1]

Anal. Calc'd for $C_{18}H_{12}Br_2O_2$: C, 51.46; H, 2.88. Found: C, 51.36; H, 2.42.

The *oxime* was prepared by the pyridine method[18] (refluxing 40 min.) and was recrystallized from ethanol, m.p. 164–164.5°.

Anal. Calc'd for $C_{18}H_{13}Br_2NO_2$: C, 49.68; H, 3.01; Found: C, 49.57; H, 3.08.

Nitric acid oxidations of 3-aroyl-(or acyl)-2,5-diarylfuran.[19]

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(18) Shriner and Fuson, *Identification of Organic Compounds*, 2nd edition. John Wiley and Sons, Inc., New York, N.Y., 1940, p. 167.

(19) Lutz and Wilder, *J. Am. Chem. Soc.*, **56**, 978 (1934).

TABLE II

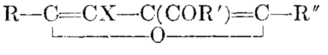
DEHYDRATIONS OF 1-MESITOYL-1,2-DIBENZOYLETHANE AND ITS ENOL

Subt.	G.	Reagents and Solvents	Conditions	Yield of XXXII	Furan, % XXXIII
XXX	0.85	2 g. $SnCl_2 \cdot 2H_2O$, 20 ml. HOAc, 4 ml. HCl^{a}	Refluxing 10 min.	68	15
XXX	0.5	1 g. $SnCl_2 \cdot 2H_2O$, 0.5 g. $SnCl_4$, 15 ml. HOAc, 3 ml. HCl^{a}	Refluxing 10 min.	80	13
XXX	0.2	5 ml. HOAc, 0.7 ml. H_2O, 2 drops HCl^{a}	Refluxing 10 min.	79	10
XXX	0.3	10 ml. HOAc, 1.4 ml. H_2O, 3 drops HCl	25–30°, 30 min.	^{b}	^{b}
XXX	1	10 ml. Ac_2O, 2 drops H_2SO_4	25–30°, 15 min.	10^{c}	70^{c}
XXX	0.25	5 ml. Ac_2O, 1 ml. H_2SO_4	25–30°, 15 min.	^{d}	^{d}
XXX	0.3	5 ml. Ac_2O, 1 drop H_2SO_4^{a}	110–115°, 10 min.	9	72
XXIX	1	2 g. $SnCl_2 \cdot 2H_2O$, 20 ml. HOAc, 4 ml. HCl^{a}	Refluxing 10 min.	81	14
XXIX	1	10 ml. Ac_2O, 2 drops H_2SO_4	25–30°, 15 min.	13	76

[a] The nearly boiling reagents were added to the saturated triketone or enol and the mixtures were heated rapidly to refluxing temperature. HCl, AcOH and H_2SO_4 are "concentrated." [b] No reaction occurred under these conditions; XXX was recovered in 93% yield. [c] Very similar results were obtained in duplicated runs. [d] The products were water-soluble and sulfonation probably had occurred.

TABLE III

ULTRAVIOLET ABSORPTION SPECTRA[a,c]

R	X	R′	R″	λ_{max}, mμ		$\epsilon \times 10^{-3}$		λ_{min}, mμ		$\epsilon \times 10^{-3}$	
		RCOCX=C(COR′)COR″									
C_6H_5	H	C_6H_5	C_6H_5^{4}	252.5	283^{s}	25.2	15.0				
C_6H_5	H	p-BrC_6H_4	C_6H_5 (*cis*)	251	271^{s}	25.2	23.6				
			At photoequilibrium^{d}	257	285^{s}	24.6	10.8	237		20.6	
C_6H_5	H	p-BrC_6H_4	C_6H_5 (*trans*)	264		29.9		229		17.0	
			At photoequilibrium^{d}	257	285^{s}	24.4	10.9	237		21.0	
C_6H_5	Cl	p-BrC_6H_4	C_6H_5 (*cis*)	270		33.2		231		13.0	
C_6H_5	H	C_9H_{11}	C_6H_5 (*cis*)	247	280^{s}	25.2	11.2	227		17.8	
C_6H_5	H	CH_3	C_6H_5 (*cis*)	247	279^{s}	20.1	11.0				
p-BrC_6H_4	H	CH_3	p-BrC_6H_4 (*cis*)	258	288	23.2	16.0	229		14.8	
		RCOCHXCH(COR′)COR″									
C_6H_5	H	C_6H_5	C_6H_5^{4}	247.5	282^{s}	40.2	3.5				
		After addition of excess KOH^{e,f,4}		234	345	24.4	10.0	290		3.7	
C_6H_5	H	p-BrC_6H_4	C_6H_5	252		39.6					
		After addition of excess KOH^{f,g}		240	340^{b}	30.9	3.95	303		2.6	
		Pure enol in isoöctane		248	317	29.4	7.6	285		5.7	
		Enol in isoöctane after 30 min.		249	310^{s}	33.2	2.6				
p-BrC_6H_4	H	C_6H_5	C_6H_5	253		42.5					
		After addition of excess KOH^{f,g}		250	335^{b}	26.6	2.6	303		1.8	
C_6H_5	Cl	p-BrC_6H_4	C_6H_5	257		42.3		228		10.6	
		After addition of excess KOH^{f}		238	338	26.6	5.0	305		3.6	
		Then acidified with HCl^{h,i}		249		29.6					
C_6H_5	Br	p-BrC_6H_4	C_6H_5	260		39.8		230		10.5	
		After addition of excess KOH^{f}		238	336	27.4	4.9	305		3.6	
		Then acidified with HCl^{h,i}		249		29.2					
C_6H_5	H	C_9H_{11}	C_6H_5	246		28.3		224		12.3	
		After addition of excess KOH^{f,g}		230	310	20.8	16.1	273		5.7	
		The pure enol form		244	306	16.9	12.7	226		6.8	
C_6H_5	Cl	C_9H_{11}	C_6H_5	253		30.4		227		9.0	
C_6H_5	H	CH_3	C_6H_5	246	280^{s}	26.3	2.7				
		After addition of excess KOH^{f,g}		237	310	19.0	8.2	260		5.6	
C_6H_5	H	p-$CH_3OC_6H_4$	C_6H_5^{j}	249	281	29.9	20.0	265		16.0	
		After addition of excess KOH^{f,g,k}		236	345^{b}	25.5	4.9	306		3.0	
		$RCOCH_2CX(COR')COR''$									
C_6H_5	Br	p-BrC_6H_4	C_6H_5	255		27.7					
		 $R{-}C{=}CX{-}C(COR'){=}C{-}R''$ (O bridge)									
C_6H_5	H	C_6H_5	C_6H_5^{3}	245	299	20.4	26.7	237	269	19.8	15.9
C_6H_5	H	p-BrC_6H_4	C_6H_5	277	297	25.2	26.0	240	280	15.6	24.8
C_6H_5	Cl	p-BrC_6H_4	C_6H_5	273	298	27.4	25.8	246	290	14.0	25.4
C_6H_5	Br	p-BrC_6H_4	C_6H_5	273	298^{s}	28.0	25.0	242		14.4	

C_6H_5	$OCOCH_3$	p-BrC_6H_4	C_6H_5	275	296	26.8	27.8	245	280	16.0	26.6
C_6H_5	H	C_6H_5	p-BrC_6H_4	252	302	22.9	25.5	233	271	19.3	16.0
C_6H_5	Cl	C_6H_5	p-BrC_6H_4	252	310	24.6	26.1	275		14.3	
C_6H_5	$OCOCH_3$	C_6H_5	p-BrC_6H_4	252	304	23.1	26.3	233	273	19.2	16.2
p-BrC_6H_4	H	C_6H_5	C_6H_5	247	308	20.4	29.8	241	270	20.0	13.6
C_6H_5	H	p-$CH_3OC_6H_4$	C_6H_5	226	297	25.0	37.4	255		8.4	
C_6H_5	H	CH_3	C_6H_5	288	328[s]	19.5	10.7	250		7.8	
C_6H_5	H	C_9H_{11}	C_6H_5	288	342	22.7	8.8	255	329	11.5	8.2
C_6H_5	Cl	C_9H_{11}	C_6H_5	288	345[s]	24.3	6.4	257		12.8	
C_6H_5	$OCOCH_3$	C_9H_{11}	C_6H_5	286	340	25.2	6.9	255		13.6	
C_6H_5	H	C_6H_5	C_9H_{11}	281	340[s]	27.1	2.9	238		15.6	
p-BrC_6H_4	H	CH_3	p-BrC_6H_4	303	335	23.3	19.4	257	331	10.0	19.2
p-BrC_6H_4	H	p-BrC_6H_4	CH_3[l]	288	335[s]	30.9	3.5	235		11.1	
C_6H_5	H	OH	C_6H_5[m,n]	313[b]		18.2		252		6.2	
C_6H_5	H	OC_2H_5	C_6H_5[m,n]	305[b]		17.8		249		7.1	
C_6H_5	COOH	OH	C_6H_5[m,o]	300		18.9		251		6.8	
C_6H_5	$COOC_2H_5$	OC_2H_5	C_6H_5[m,o]	299		19.4		252		7.4	
2,5-Diphenylfuran[9]				226	324	16.2	29.2	250		1.2	
			trans-RCOCH=CHCOR″								
C_6H_5			C_6H_5[4]	269		18.8					
C_9H_{11}			C_9H_{11}[m,p,q]	235	310[b]	21.9	2.4	230	275	21.2	1.2
p-BrC_6H_4			p-BrC_6H_4[m,r]	232	292	16.8	22.9	246		15.0	
C_6H_5			C_9H_{11}[m,t]	242.5	285[s]	15.8	8.3	227		13.4	
C_6H_5			p-BrC_6H_4[m,u]	235[s]	284	13.1	19.6				
p-BrC_6H_4			C_9H_{11}[m,t]	240	291	16.4	12.3	231	270	16.0	10.3

[a] All spectra were determined in 0.00005 *M* absolute ethanol using a Beckman DU quartz spectrophotometer. [b] The bands carrying this superscript are unusually broad. [c] C_9H_{11} denoted mesityl; references given in table are to earlier determinations of ultraviolet absorptivities. [d] Unstable photoequilibrium was achieved after the solution was exposed under a General Electric R.E. Sunlamp for 15 min. It gave a sharper and relatively lower absorption band as compared with the *cis* or *trans* isomer. The data indicated that the mixtures contained a certain amount of saturated ketones which presumably were formed by reduction, polymerization, or addition of ethanol (*cf.* ref. 4). [e] The compound shows also a shoulder at 277 mμ, ε 4,300. [f] Three drops of 10% aqueous potassium hydroxide solution were added to *ca.* 90 ml. of spectra solution. [g] The longer wave length band is apparently due to the enolate; acidification of the basified solution causes ketonization and restores almost exactly original spectra; *cf.* ref. 4. [h] Three drops of conc'd hydrochloric acid were added to the above solution. [i] That acidification of the basified solution failed to restore the original absorption is probably due to the dehydrohalogenation and addition of ethanol caused by base; *cf.* ref. 4. [j] The longer wave length band (281 mμ) is apparently due to the *p*-anisoyl group. *Cf.* Lutz and Baker, *J. Org. Chem.*, **21**, 49 (1950). [k] It also shows a relatively high shoulder at 275 mμ, ε 11,600; which indicated that enolization may not involve the *p*-anisoyl group. [l] The compound shows a shoulder at 283 mμ, ε 21,200. [m] The m.p. of samples used matched closely those reported in the literature. [n] Prepared according to ref. 14a. [o] Prepared according to ref. 14b. [p] In isoöctane it showed λ_{max} 235 and 300 mμ (the latter very broad) ε 20,800 and 2,400; the previously reported spectrum[2d] involves a typographical error. [q] Conant and Lutz, *J. Am. Chem. Soc.*, **45**, 1303 (1923). [r] Conant and Lutz, *J. Am. Chem. Soc.*, **47**, 881 (1925). [s] These values represent shoulders rather than distinct bands. [t] Lutz and Boyer, *J. Am. Chem. Soc.*, **63**, 3189 (1941). [u] Kohler and Woodward, *J. Am. Chem. Soc.*, **58**, 1933 (1936).

cis-1-Mesitoyl-1,2-dibenzoylethylene (XXVIII) from XXXIII at 5–10° (20 min.), yield 82%; crystallized from methanol, m.p. 111–112°.

Anal. Calc'd for $C_{26}H_{22}O_3$: C, 81.65; H, 5.80. Found: C, 81.82; H, 6.05.

cis-1-Acetyl-1,2-dibenzoylethylene (Ic) was prepared by the nitric acid-propionic acid oxidation of Vc at 0° for 15 min., yield 85%; it was crystallized from methanol, m.p. 114–115°.

Anal. Calc'd for $C_{18}H_{14}O_3$: C, 77.68; H, 5.07. Found: C, 77.50; H, 5.00.

cis-1-Acetyl-1,2-di-(p-bromobenzoyl)-ethylene (Id) was formed by the nitric acid oxidation of Vd at 10–15° (25 min.), 77% yield; it was crystallized from a benzene-methanol mixture, m.p. 151–152°.

Anal. Calc'd for $C_{18}H_{12}Br_2O_3$: C, 49.57; H, 2.77. Found: C, 49.65; H, 2.87.

Attempts to prepare 1-anisoyl-1,2-dibenzoylethylene (Ie) by the nitric-propionic acid oxidation of Ve at 0–5° for 10 min. or at −18 to −20° for 30 min., gave only oils, from which the saturated triketone could be obtained on reduction.

Stannous chloride reduction of unsaturated triketones. 3-Benzoyl-2-mesityl-5-phenylfuran (XXXII). One gram of XXVIII was reduced by stannous chloride according to the method described for Ia and IIa. Fractional crystallization of the products from isopropyl alcohol gave 0.29 g. (30%), of furan Vb and 0.48 g. (50%) of the new isomeric furan (XXXII). M.p. of XXXII, after recrystallizations from ethanol, 124–125°; it gave a 25° mixture m.p. depression with XXXIII.

Anal. Calc'd for $C_{26}H_{22}O_2$: C, 85.21; H, 6.05. Found: C, 85.14; H, 6.03.

In a duplicated reduction under the same conditions 1 g. of XXVIII gave 0.31 g. (32%) of XXXIII and 0.41 g. (43%) of XXXII.

Treatment of XXVIII *with conc'd hydrochloric in acetic acid* (1:5) (this represents 1.6 *N* HCl in 86% AcOH) without stannous chloride (refluxing 10 min.) gave 28% of unchanged XXVIII and intractable oil.

3-(p-Bromobenzoyl)-2-methyl-5-(p-bromophenyl)furan (VId). Stannous chloride reduction of 2 g. of Id (as above) gave 0.63 g. (33%) of the furan Vd and 1.05 g. (55%) of a new isomer VId which melted at 132.5–134° after repeated recrystallizations from ethanol. VId gave a 30° mixture m.p. depression with Vd.

Anal. Calc'd for $C_{18}H_{12}BrO_2$: C, 51.46; H, 2.88. Found: C, 51.76; H, 3.25.

The *oxime* of VId was prepared by the pyridine method[18] (refluxing 2 hours); it was recrystallized from ethanol, m.p. 183–185°.

Anal. Calc'd for $C_{18}H_{13}Br_2NO_2$: C, 49.68; H, 3.01. Found: C, 49.31; H, 2.90.

Attempted reductions of Ic and Ie by stannous chloride (as above) only gave intractable oils.

Sodium hydrosulfite reduction of unsaturated triketones. 1-Mesitoyl-1,2-dibenzoylethane (XXX). Reduction of 0.8 g.

of XXVIII with sodium hydrosulfite in 70% ethanol (refluxing 30 min.) produced an oil which gave a deep red color test with ethanolic ferric chloride. It gradually crystallized from methanol after standing for several days and was recrystallized from methanol; 0.34 g. (43%); m.p. 142–143°. The purified product gave no color test with ferric chloride.

Anal. Calc'd for $C_{26}H_{24}O_3$: C, 81.22; H, 6.29. Found: C, 81.24; H, 6.16.

A *copper enolate* was prepared[3b] from XXX, m.p. 240–242°.

Anal. Calc'd for $C_{52}H_{46}CuO_6$: Cu, 7.65. Found: Cu, 7.41.

An *enol* XXIX was obtained by treatment of the copper enolate with ether-dilute aqueous hydrochloric acid mixture and subsequent evaporation of the ether extract; it was crystallized from an ether-petroleum ether mixture, m.p. 112–114°.

Anal. Calc'd for $C_{26}H_{24}O_3$: C, 81.22; H, 6.29. Found: C, 81.38; H, 6.24.

It gave a deep red color test with alcoholic ferric chloride and showed a 10° depression of mixture m.p. with XXX. On standing in acidic ethanol solution the enol reverted to XXX in nearly quantitative yield.

Dehydration of XXX *and its enol* XXIX under different conditions of temperature, reagent, and solvent gave various ratios of furans XXXII and XXXIII. In a typical run, the solution of products was hydrolyzed (or diluted) with ice-water and the resulting oil was extracted with benzene. After evaporation of the benzene, the furans were separated by fractional crystallization from methanol or ethanol and were identified by mixture m.p. The results of a series of experiments are listed in Table II.

1-Acetyl-1,2-dibenzoylethane IVc was prepared by reduction of Ic with sodium hydrosulfite in dilute ethanol as above; it was crystallized from methanol, m.p. 88.5–89.5°. It gave no color test with ferric chloride. (Bodforss[20] reported m.p. 88–89° and a red color test with ferric chloride).

Anal. Calc'd for $C_{18}H_{16}O_3$: C, 77.12; H, 5.75. Found: C, 77.17; H, 5.72.

A *copper enolate* was prepared[3b] from IVc, m.p. 192–193°.

Anal. Calc'd for $C_{36}H_{30}CuO_6$: Cu, 10.21. Found: Cu, 9.70.

Acidification failed to give the enol; only IVc was obtained.

Attempted *dehydration of IVc* with acetic anhydride and sulfuric acid gave only oils.

1-p-Anisoyl-1,2-dibenzoylethane (IVe) was prepared from the oily unsaturated triketone Ie by sodium hydrosulfite reduction as above; yield 67%; it was crystallized from a benzene-ethanol mixture, m.p. 111–112°. It gave no ferric chloride color test.

Anal. Calc'd for $C_{24}H_{20}O_4$: C, 77.40; H, 5.41. Found: C, 77.48; H, 5.49.

Attempted *dehydration of IVe* with acetic anhydride and conc'd sulfuric acid gave only an oil.

Attempts to prepare 1-acetyl-1,2-di-(p-bromobenzoyl)ethane (IVd) by sodium hydrosulfite reduction (as above) produced an oil which gave a red color test with ferric chloride. On longer standing, only a small amount of 1,2-di-(*p*-bromobenzoyl)ethane and *p*-bromobenzoic acid were isolated (identified by mixture m.p.), and the oily product no longer gave a color test with ferric chloride.

Dehydration of 1 g. of the saturated triketone IVd (oil) with *acetic anhydride* and *conc'd sulfuric acid* in the usual way (room temperature, 15 min.) gave 0.17 g. (18%) of Vd and 0.40 g. (42%) of VId. Treatment of 1 g. of IVd with a *stannous chloride-conc'd hydrochloric-acetic acid* mixture (1.6 *N* HCl–86% AcOH) (refluxing for 10 min.) gave 2.1 g. (22%) of Vd and 0.33 g. (34%) of VId.

Zinc reduction of XXVIII (1 g.) in 40 ml. of conc'd acetic acid, 40 ml. of ether, and 4 ml. of water (3 g. of Zn) at −5 to 0° (20 min.), dilution with water, and treatment of the ether extract with aqueous copper acetate, gave 0.15 g. of the copper enolate of XXIX, m.p. 239–241° (identified by mixture m.p.). The corresponding saturated triketone XXX after subjection to the same conditions was recovered nearly quantitatively.

Addition compounds of unsaturated triketones. 1-Mesitoyl-2-morpholinyl-1,2-dibenzoylethane (IIIb;h) was prepared by treatment of Ib with morpholine in ether solution (10 min.) and subsequent evaporation of the solvent; it was recrystallized from 1:10 ethanol-ether, m.p. 137–138°, yield 82%. It gave no ferric chloride color test.

Anal. Calc'd for $C_{30}H_{31}NO_4$: C, 76.73; H, 6.65. Found: C, 76.42; H, 6.56.

1-Acetyl-2-morpholinyl-1,2-dibenzoylethane (IIIc;h) was prepared as above; it was crystallized from ethanol, m.p. 125–126°, yield 55%.

Anal. Calc'd for $C_{22}H_{23}NO_4$: C, 72.31; H, 6.34. Found: C, 72.23; H, 6.26.

1-Mesitoyl-2-chloro-1,2-dibenzoylethane (XXXI). Compound XXVIII (2 g.) was treated with 100 ml. of 9% hydrogen chloride in dry ether. After standing at room temperature for 28 hours, the solution was evaporated and the residue was crystallized from an ethyl acetate-ethanol mixture; 1.54 g. (70.5%); colorless, m.p. 174–175° (decomp.).

Anal. Calc'd for $C_{26}H_{23}ClO_3$: C, 74.54; H, 5.53. Found: C, 74.27; H, 5.52.

Dehydrohalogenation of XXXI with triethylamine in ether solution (room temperature, 24 hrs.) gave 87% of XXVIII, m.p. 105–108°.

Treatment of XXXI *with stannous chloride* according to the method described for the reduction of XXVIII gave a mixture of XXXII (43%) and XXXIII (38%) (separated by fractional crystallization and identified by mixture m.p.). Treatment of XXXI with a 5:1 acetic-hydrochloric acid mixture without the stannous chloride (1.6 *N* HCl–86% AcOH) (refluxing 10 min.) gave 6% unchanged XXXI and 48% of unsaturated triketone XXVIII.

Attempts to prepare unsaturated triketones isomeric with Ib(XXVIII), Ic, and Id by (*a*). Sunlight isomerization with or without iodine, in acetone or chloroform, gave starting material or intractable oil. (*b*). Nitric acid oxidation of the furan XXXII failed to give a solid derivative; hydrogen peroxide oxidation[3c] of XXXII also gave an oil, and 12% of XXVIII; nitric acid oxidation of VId gave oil and a small amount of Id and *p*-bromobenzoic acid. (*c*). Deamination of IIIb;h and IIIc;h by heating with dilute hydrochloric acid for several min. gave XXVIII and Ic in yields of 79% and 90%; identifications were by mixture m.p.

4-Acetoxy-3-mesitoyl-2,5-diphenylfuran (XXXV). (*a*). A mixture of 1 g. of XXVIII, 15 ml. of acetic anhydride, and one drop of conc'd sulfuric acid was allowed to stand at 0° for 10 min. The dark red solution was hydrolyzed with ice-water and the resulting oil was extracted with ether. Evaporation and crystallization of the residue from methanol gave 0.92 g. (83%), colorless, m.p. 136–137°.

Anal. Calc'd for $C_{28}H_{24}O_4$: C, 79.22; H, 5.70. Found: C, 79.25; H, 5.62.

(*b*). A mixture of 1 g. of XXXIII and 2 g. of lead tetraacetate in 20 ml. dry acetic acid was refluxed for 10 min. and poured into ice-water. Crystallization of the product from methanol gave 0.14 g. (12%) of XXXV (identified by mixture m.p.).

4-Chloro-3-mesitoyl-2,5-diphenylfuran (XXXVI). (*a*). One gram of furan XXXIII was treated with 3 g. of phosphorus pentachloride at 120–125° for 25 min. The mixture was hydrolyzed with ice-water. Fractional crystallization of the product from isopropyl alcohol gave 0.24 g. (24%) of unchanged XXXIII and 0.22 g. (20%) of XXXVI; m.p. after treatment with charcoal and recrystallization from ethanol, 109–110°.

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[20] Bodforss, *Ber.*, **51**, 199 (1918).

Anal. Calc'd for $C_{26}H_{21}ClO_2$: C, 77.89; H, 5.28. Found: C, 77.89; H, 5.62.

(*b*). A mixture of 1.5 g. of XXVIII and 25 ml. of acetyl chloride was treated with 3 drops of conc'd sulfuric acid (0–5° for 6 min.) and hydrolyzed with ice-water. Fractional crystallization from isopropyl alcohol gave 0.25 g. (15%) of XXXV, m.p. 122–126° and 0.91 g. (57%) of XXXVI, m.p. 106–108° (identified by the mixture m.p.).

Oxidation of XXXVI with nitric-acetic acid at 0–5° or 25–30° gave only unchanged XXXVI, and at 50–60° (30 min.) gave an oil.

Attempts to prepare 4-chloro-3-benzoyl-2-mesityl-5-phenylfuran by treatment of XXXII with excess phosphorus pentachloride (120–125°, 45 min.) gave an oil which when oxidized with a nitric-acetic acid mixture also gave an oil.

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