

THE CONFIGURATIONS OF THE ALKOXY-1,2-DIBENZOYL-ETHYLENES AND RELATED COMPOUNDS¹ROBERT E. LUTZ AND SPENCER M. KING²

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Recent studies on the *cis*- and *trans*-1,2-dibenzoylethylenes and benzalacetophenones (2-4) are of interest in connection with the possibility of assignment of configurations to the alkoxy, aroxy, hydroxy, amino, and alkylamino-dibenzoylethylenes (I, II, VIII, IX), and have led to the further work described in this paper.

Methoxydibenzoylethylene (I) (5-9), known in only one form, has been regarded (probably correctly) as thermodynamically the more stable of the two possible stereoisomers, and because of this it was considered to be *trans* (7). However, its synthesis by nitric acid oxidation of the corresponding furan suggests the *cis* configuration (9, 10).

Positive evidence on which to base configurational assignments was sought through study of cases where both stereoisomers could be obtained and compared.

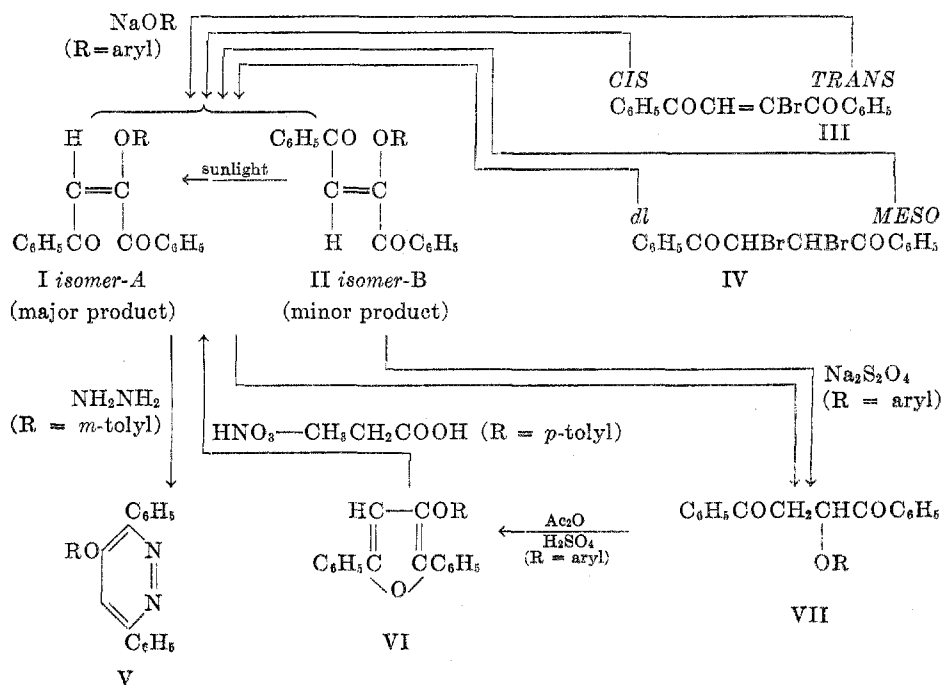
To date only 3-methylphenoxydibenzoylethylene has been obtained in two stereoisomeric forms (6). The preparation of these isomers from *meso*-dibenzoylethylene dibromide (IV) by the action of sodium 3-methylphenoxide has been repeated; and similar pairs of isomers have now been obtained using sodium phenoxide and 4-methylphenoxide. No second forms of any of the alkoxy-dibenzoylethylenes have yet been found. In all cases where two isomers have been isolated, the main product has been the higher-melting of the two (isomer-A; colorless; yields 30-85%) and the minor isomer has been the lower-melting (B; pale yellow, giving definitely yellow solution; yields 4-23%).

It was hoped that some stereospecificity might appear in the preparations using the *dl*- and *meso*-dibromides (IV) and the *cis*- and *trans*-bromodibenzoylethylenes (III), and that a good way might be found to produce the minor isomer in quantity. Some slight improvement in the yield of the minor isomer was effected but little evidence of significant if any differences in the ratios of products was observed in the few tests under comparable conditions on the four starting materials III-IV; consequently only limited work was done. In the *para*-methylphenoxy series at a reaction temperature of 2-10° the chief product was the higher-melting isomer-A and the lower-melting isomer-B was actually isolated in small amounts from the *dl*- but not from the *meso*-dibromide (IV); from the reactions under these same conditions with *cis*- and *trans*-bromodibenzoylethylenes (III) the isomer-A was the main product and in both cases there were obtained small amounts of mixtures which doubtless contained some of the lower-melting isomer-B.

¹ The work on which this paper is based is described in ref. (1).

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The various aroxydibenzoylethylenes were reduced to the corresponding aroxydibenzoylethanes (VII). Two of the latter, the phenoxy- and 4-methylphenoxydibenzoylethanes, were converted to the furans (VI) by the action of acetic anhydride and sulfuric acid, but the 2- and 3-methylphenoxyfurans were not obtained by this type of reaction, nor could they be obtained directly from the aroxydibenzoylethylenes under conditions usually effecting reductive furanization. In this connection it should be noted that methoxydibenzoylethylene is reductively furanized by zinc and acetic acid but methoxydibenzoylethane has not successfully been furanized by acetic anhydride and sulfuric acid (6).



The facile formation of a pyridazine by the action of hydrazine hydrate on a *cis* unsaturated 1,4-diketone and the difficulty of reaction with the *trans* isomer under the same conditions has been used to distinguish between stereoisomers and to characterize the *cis* form (11, 12). Application of the method here indicates unmistakably, in the one case successfully studied, that the higher-melting *meta*-methylphenoxydibenzoylethylene-A is the *cis*-isomer (I), because only this isomer gives the pyridazine (V).

The nitric acid oxidation of an aroxyfuran to an aroxydibenzoylethylene was successful only in the case of the 4-methylphenoxy compound, and this reaction offers a sound chemical basis for assignment of *cis* and *trans* configurations in this one case. The compound obtained in this oxidation is identical with the higher-melting isomer-A, which is the major product of the reaction between

sodium 4-methylphenoxide and the dibenzoylene dibromides and bromo-dibenzoylethylenes. The lower-melting and minor isomer-B is stable under these oxidizing conditions and if it had been formed in significant amounts during the oxidation it would have been detected. Thus it is established by ring-cleavage that the higher-melting isomer in this case actually is *cis*. It follows by seemingly safe analogy that the products of oxidations of other aroxy and alkoxy furans also are *cis*.

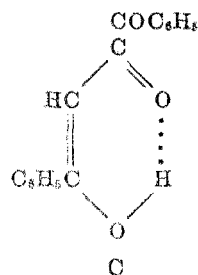
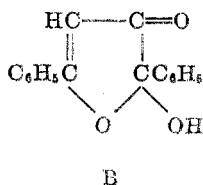
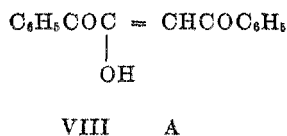
The ultraviolet absorption spectra listed in Table I closely resemble the absorptions of the dibenzoylethylenes and their monobromo and monomethyl derivatives. In those cases where both *cis* and *trans* isomers have been obtained the dominant isomers, which are the higher-melting and less-soluble (*cis*) forms, show in ethanol absorption maxima at 261–262 $m\mu$ and extinction coefficients of *ca.* 25×10^3 , whereas the minor and low-melting (*trans*) isomers show slightly higher maxima of 265–266 $m\mu$ but significantly lower extinctions of *ca.* 20×10^3 . In those cases where only one form has been isolated, the *cis* configuration, corresponding with that of the dominant higher-melting isomers where pairs are known, may therefore tentatively be assigned by analogy on the basis of the slightly low absorption maxima (261–262 $m\mu$) and high extinction coefficients ($24\text{--}25 \times 10^3$). Incidentally it is evident from these results that the positive-heteroelement resonance forms of the oxybenzalacetophenone systems are not particularly important here, as is the case with the 3-alkoxy- and 3-aroxy-2,5-diphenylfurans (VI), but in contrast with the nitrogen analogs of the type IX and with 3-morpholinyl-2,5-diphenylfuran (13, 14) where positive-nitrogen forms produce very significant effects.

Scale drawings based on van der Waals' radii analogous to those of other substituted dibenzoylethylenes given in a previous paper (2), indicate that the *cis* arrangement is slightly the more favorable here as in the case of methyl- and bromo-dibenzoylethylenes. The presumably small positive-oxygen resonance contribution would doubtless affect somewhat the effective interference radius of the oxygen and would tend to align the oxygen and its substituent in some degree of coplanarity with the dibenzoylene system. The *cis* isomers consequently should have the higher extinction coefficient. Assignment of configuration on this basis is consistent with the assignment based on pyridazine formation and on the relation to furans by oxidative ring cleavage.

It has not yet been shown directly by chemical means which of the isomers actually are the stable forms. The compounds are sensitive toward hydrolytic type conditions. The lower-melting aroxydibenzoylethylenes are converted by sunlight irradiation of ethanol solutions into the higher-melting isomers, (*cf.* Ref. 6 for the 3-methylphenoxy compound). But neither isomer was isomerized by sunlight irradiation of a chloroform solution containing a trace of iodine. The successful sunlight transformation in which no obvious catalyst was used is not significant by itself, and it may be analogous to the sunlight isomerization of the labile *trans*-methyl-dibenzoylene to the more stable *cis* form (15).

Hydroxydibenzoylene (VIII A), obtained by the action of sodium hydroxide on dibenzoylene dibromide or methoxydibenzoylene (7, 16–

18), is yellow in solution and exists in two solid forms. One of these (yellow; m.p. 66–67°) is soluble in isooctane. The other (m.p. 88–90°) is colorless and changes to the yellow form upon fusion and resolidification. The latter isomer does not melt under boiling isooctane (100°), and when small portions are added to stirred mineral oil at increasing temperatures, fusion of the crystals is not observed until the temperature of the medium reaches 135°. It appears that the hydrocarbon solvent in which the colorless form is very difficultly soluble tends to remove from the surface of the crystals the more soluble yellow form as fast as it is produced and thus prevents acceleration of the fusion; the true melting point of the colorless form is therefore considerably higher than had previously been supposed.



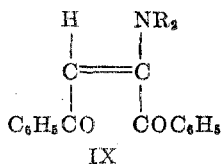
It has been suggested that the two forms of hydroxydibenzoyl ethylene are ring-chain tautomers (VIII B, C) although the possibility of crystal dimorphism has not been excluded. The identity of ultraviolet absorptions immediately upon solution of the two solid forms in ethanol showed that if tautomerism is the explanation the transition from one to the other in solution is very rapid. The two absorption peaks at 245 $\text{m}\mu$ (ϵ , 13.6×10^3) and 318 $\text{m}\mu$ (ϵ , 14.6×10^3), perhaps fortuitously, resemble those of 2-methoxy-2,5-diphenylfuranone-3 where however the extinction at the shorter wave length band (247 $\text{m}\mu$) is significantly lower (8.5×10^3) and is higher at the longer wave length band (314 $\text{m}\mu$; ϵ , 17.4×10^3) (13). Methoxydibenzoyl ethylene on the other hand has a single peak of λ_{max} 261 $\text{m}\mu$ (ϵ , 24.5×10^3). There is a striking increase in wave length of both absorption maxima of hydroxydibenzoyl ethylene upon going from ethanol solution to the less polar isooctane in which the colorless form is very difficultly soluble. These results are not inconsistent with the assumption that a mobile equilibrium exists in solution between the hydroxyfuranone (VIII B) and a dominant open-chain and presumably chelated enol (VIII C), but the chelated enol structure, it should be noted, would presumably involve a *trans* structure with respect to the hydroxydibenzoyl ethylene system.

The amino, alkylamino, and dialkylaminodibenzoyl ethylenes (IX) each occur in only one form (6, 13,³ 19), which is presumed to be the stable one. To our knowledge no authenticated examples of *cis-trans* isomerism in other related series involving the system $\text{---COC}=\text{C---N}$ have yet been reported (20–22).⁴

³ In ref. 13 dealing with the preparation of aminodibenzoyl ethylenes, the % yield of methylaminodibenzoyl ethylene of 25% should read 2.5% (see pages 184, 193, and 198).

⁴ *Cis-trans* isomerism of this type has been postulated in two cases. One of these is

From a study of the planar diagram based on van der Waals' radii, assuming a significant contribution by positive-nitrogen resonance forms and a consequent tendency toward planarity of the NR_2 group with the dibenzoyl ethylene system, it may be concluded that these compounds which involve tertiary nitrogen are *cis* (IX) because in this arrangement there would be a minimum overlap of groups.



The fact that nitric acid oxidized 2,5-diphenyl-3-morpholinylfuran to the morpholinyl dibenzoyl ethylene (19) supports this assignment of the *cis* configuration, but in the absence of the stereoisomer for stability test under the oxidizing conditions this reaction does not constitute rigorous proof.

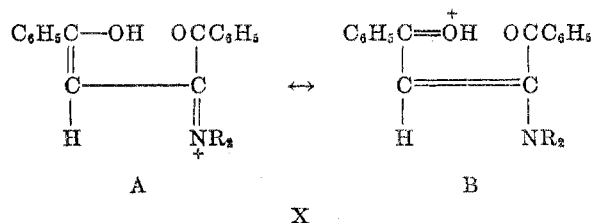
The ultraviolet spectral data for all of these compounds including the secondary amino types but excepting the primary amino derivative where $\text{NR}_2 = \text{NH}_2$, seem to be consistent in the main with the assumption of *cis* configurations. A scale planar diagram based on van der Waals' radii shows for the parent aminodibenzoyl ethylene a minimum overlap in the *trans* arrangement; however, this compound has an exceptionally low benzoyl type absorption (λ_{max} 260 μ ; ϵ , 1.8×10^3), and the position of the longer wave length band is exceptional and is at the longest wave length of the series (λ_{max} 370 μ ; ϵ , 11×10^3). The introduction of one methyl, two methyls, or phenyl, on the nitrogen of the aminodibenzoyl ethylene, would be expected sharply to increase steric interference with planarity much more than happens in the vinyl phenyl ketone series (20),⁵ $\text{C}_6\text{H}_5\text{COCH}=\text{CHNR}_2$. This effect conceivably might account here for the lack of regular bathochromic shift of absorption maxima toward longer wave length in the series $-\text{NH}_2$, $-\text{NHCH}_3$, and $-\text{N}(\text{CH}_3)_2$, but the exceptional nature of the absorption of the amino compound suggests that it involves a structural or configurational difference.

The mono- and di-methylamino groups both involve sharp lowering of the longer wave length maxima to 334 and 346 μ respectively, but there is at

$\text{CH}_3\text{COCH}=\text{CHNHC}_6\text{H}_5$ (21) but lack of any significant difference in the ultraviolet absorption spectra of the two forms suggests that possibly dimorphism is the explanation. In the other case, $\text{C}_6\text{H}_5\text{COCH}=\text{CHNH}_2$ (20), the data can be interpreted in terms of solvation in one form (β). The two forms absorb at identical wave lengths. The α -form (sublimed; m.p. 83°) has the higher absorbing power whereas the β -form (m.p. 90-91°; analyzed only for nitrogen) shows lowerings of extinction coefficients at both λ_{max} which correspond closely to the calculated dilution effect that would be caused by one molecule of alcohol of solvation.

⁵ We believe that these β -aminovinyl ketones may reasonably be presumed to be *trans* since these would be the stable forms, and that they correspond in configuration to the (substituted-amino)-dibenzoyl ethylenes which, while *cis* with respect to the benzoyls, are *trans* with respect to one benzoyl and the amino group *beta* to it.

the same time a sharp and in this case progressive increase in extinction coefficients, not only of the longer wave length band but also of the benzoyl type band in the 260 $m\mu$ region. In the anilindibenzoylethylene series the N-phenyl and N-*p*-xenyl groups cause a marked shift of the longer wave length band to 375 and 384 $m\mu$ respectively, but the additional substitution of an N-methyl brought the maxima down to 342 and 345 $m\mu$ respectively, thus offsetting the conjugational effect of the phenyls, presumably by steric interference with planarity.



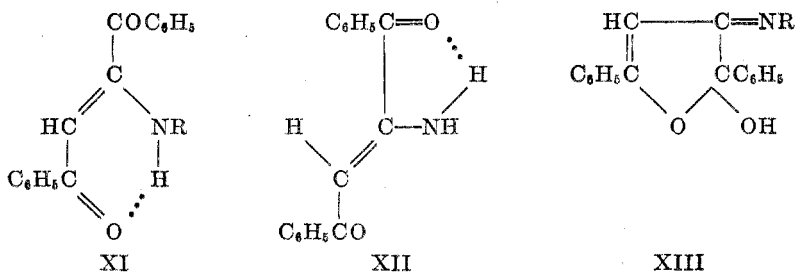
The effect of 1.0 *N* hydrogen chloride on the ultraviolet absorption of dimethylaminodibenzoylethylene in ethanol (Table I) involves a significant shift of both maxima to longer wave lengths and suggests the formation of a resonance-stabilized cation (*cf.* X). The hydrochloride of this compound, alone without excess acid, shows little of this effect, doubtless because this salt is unstable, (*e.g.*, it is readily hydrolyzed by water).

TABLE I
ULTRAVIOLET ABSORPTIONS OF $\text{C}_6\text{H}_5\text{COCH}=\text{C}(\text{X})\text{COC}_6\text{H}_5$

X	ISOMER	M.P., °C.	ABSORPTION			
			in abs. ethanol		in isoctane ^a	
			λ_{max} , $m\mu$	$\epsilon \times 10^{-3}$	λ_{max} , $m\mu$	$\epsilon \times 10^{-3}$
OCH_3	<i>cis</i> ^b	108.5	261	24.5	—	—
OC_6H_5	<i>cis</i>	92	262	24.5	258	25.5
	<i>trans</i>	87	266	20.3	260	18.7
O-(2-methylphenyl)	<i>cis</i> ^b	95.5	262	25.2	—	—
O-(3-methylphenyl)	<i>cis</i>	102	262	24.3	257	24.0
	<i>trans</i>	95.5	266	20.5	260	21.1
O-(4-methylphenyl)	<i>cis</i>	167.5	261	24.6	257	25.5
	<i>trans</i>	101.5	265	21.0	260	21.9
OH		90(135)	245	13.6	258	9.3
		67	318	14.6	340	14.0
$\text{N}(\text{CH}_3)_2$	<i>cis</i> ^b	165	254	21.0	—	—
			340	17.5	—	—
$\text{N}(\text{CH}_3)_2 \cdot \text{HCl}$ ^c	<i>cis</i>		258	14.5	—	—
			348	18.8	—	—
$\text{N}(\text{CH}_3)_2$ in 1.0 N HCl	<i>cis</i>		270	10.0	—	—
			(358 ^d)	(25.0)	—	—
			363	25.7	—	—

^a Isooctane = 2,2,4-trimethylpentane. ^b Presumed configuration; the stereoisomer is unknown. ^c The salt doubtless is largely alcoholized under these conditions. ^d This is an inflection point.

It is worthy of note that in the methylamino and dimethylamino compounds (but not the parent amino compound) the ultraviolet absorption maxima correspond strikingly with expectations deduced from scale planar drawings based on van der Waals' radii and the assumption of two effective chromophores, the β -amino vinyl phenyl ketone system (*cf.* λ_{\max} of 334 and 340 $m\mu$ and ϵ , 14 and 17.5×10^3 as compared with λ_{\max} of 338 and 343 $m\mu$ and ϵ , 23 and 26×10^3 for the parent β -N-ethylamino and diethylamino vinyl phenyl ketone analogs), and the *cis* dibenzoyl ethylene system (*cf.* λ_{\max} 253 and 254 $m\mu$, ϵ , 14 and 17.5×10^3 as compared with λ_{\max} 260 and 258, ϵ , 18 and 22×10^3 , for *cis* dibenzoyl ethylene itself and *cis* methyl dibenzoyl ethylene). There is the possibility when nitrogen is secondary or primary that a chelated *trans* structure (XI or XII⁶) or a furan imine structure (XIII) might hold. The possibility of hydrogen-bonding of an α -amino ketone such as XII is suggested by the speculations of Gero (23) in his very recent study of α -amino-*p*-hydroxyacetophenone. In the



secondary amine types, however, the close correspondence of the ultraviolet absorptions with those of the dialkylamino compounds where chelate or imine structures are impossible, strongly indicates that these compounds are analogs and have the *cis* structures (IX). On the other hand the supposition of a chelated structure (XI or XII) in the primary amino compound (where $\text{NR}_2 = \text{NH}_2$) is particularly attractive because in this one case there is exceptional divergence of both characteristic absorption bands from the characteristic bands of the secondary and tertiary nitrogen analogs including the dimethylamino compound which is taken as a standard of reference. This divergence involves a low extinction coefficient of the band in the range characteristic of a benzoyl group and a radically longer wave length and a lower extinction coefficient of the longer wave length band. This conclusion, at least with respect to the possibility of XI, is consistent with the postulated greater ability of $-\text{NH}_2$ as against $-\text{NHR}$ to take part in hydrogen bonding with the oxygen of a carbonyl group to which the nitrogen is *alpha* (23).

Further studies in this field are in progress.

EXPERIMENTAL

Phenoxydibenzoyl ethylenes-A and -B (cis and trans; I and II). Reaction between *meso*-dibenzoyl ethylene dibromide (IV) and sodium phenoxide at 30–39° gave the compound

⁶ In the *cis* forms this type of chelation would be most unlikely because it would require a sterically unfavorable arrangement of the two benzoyl groups in the all-planar arrangement required of effective conjugation.

already known (5), here to be designated as isomer-A, in 35% yield. It is now assigned the *cis* configuration (I).

dl-Dibenzoyl ethylene dibromide (IV) (9.9 g., 0.025 mole) was added to 1.7 g. (0.075 mole) of sodium and 7.5 g. (0.08 mole) of phenol dissolved in 100 ml. of absolute ethanol maintained at -20° in a cold chest for 7 days with occasional shaking. The mixture was poured into ice-water and the semi-solid mass was filtered and crystallized from methanol; 5.6 g. (68%) of isomer-A [*cis*; I (5)]; m.p. $90-92^{\circ}$. Concentration of the filtrate gave 0.8 g. (10%) of the new isomer-B (*trans*; II), m.p. $73-80^{\circ}$, which upon recrystallizations from methanol melted at $86-88^{\circ}$; light yellow.

Anal. Calc'd for $C_{22}H_{16}O_3$: C, 80.47; H, 4.91.

Found: C, 80.29; H, 4.84.

The *meso*-dibenzoyl ethylene dibromide reacted slowly under these conditions and a large proportion of the product was unchanged material.

Reduction of the *cis*- and *trans*-isomers in refluxing 75% ethanol by addition of four molecular equivalents of sodium hydrosulfite (*cf.* ref. 6) gave phenoxydibenzoyl ethane in yields of 80% and 65% respectively; m.p. $120-122^{\circ}$.

The *trans* isomer was converted to *cis* by irradiation of an ethanol solution. Neither isomer was changed by irradiation of a chloroform solution containing iodine.

(*2-Methylphenoxy*)dibenzoyl ethylene (I). Reaction between 39.6 g. of IV (*meso*) and a solution of 4.6 g. of sodium and 21.6 g. of *ortho*-cresol in 100 ml. of absolute ethanol ($30-40^{\circ}$) gave an oil which, on crystallization from ethanol, gave 18.6 g. (56%) of crude product; recrystallized from methanol; m.p. $95-96^{\circ}$. This is presumed to be the *cis* form.

Anal. Calc'd for $C_{23}H_{18}O_3$: C, 80.69; H, 5.30.

Found: C, 80.75; H, 5.12.

(*2-Methylphenoxy*)dibenzoyl ethane (VII). Reduction of 4.4 g. of I with 4.5 g. of sodium hydrosulfite in 75% ethanol under reflux for 45 min. gave 4.1 g. (93%) of VII; recrystallized from absolute ethanol, m.p. $137-139^{\circ}$.

Anal. Calc'd for $C_{23}H_{20}O_3$: C, 80.21; H, 5.85.

Found: C, 80.34; H, 5.87; H, 6.26; 5.85.

Furanization attempts (*cf.* 6) were unsuccessful.

cis- and *trans*-(*3-Methylphenoxy*)dibenzoyl ethylenes-A and -B. The preparation of the stereoisomers from *meso*-dibenzoyl ethylene dibromide (6) was successfully repeated and yields of 50% of the isomer-A (*cis*) and 4.4% of the isomer-B (*trans*) were obtained. From the *dl*-bromide the yield of isomer-A (*cis*) was 25% and of B (*trans*) 16%. The reaction of a mixture of dibenzoyl acetylene, *meta*-cresol, triethylamine, and benzene under reflux gave a 31% yield of the *cis* isomer (I). Both isomers were reduced to the same saturated diketone by sodium hydrosulfite in 75% ethanol. Attempts to isomerize from *cis* to *trans* by the action of benzene and hydrochloric acid (refluxing), iodine in chloroform, and benzene and hydrochloric acid (sunlight), were unsuccessful. The *trans* isomer was rearranged to *cis* by sunlight irradiation of an ethanol solution (3e) but not by irradiation of an iodine-chloroform solution. Attempts to furanize the saturated diketone and to reductively furanize the unsaturated diketones, were unsuccessful (*cf.* 6). Attempts to oxidize the furan to the *cis* unsaturated diketone also were unsuccessful.

3,6-Diphenyl-4-(3-methylphenoxy)pyridazine (V). Hydrazine hydrate (0.2 g.) was added to a hot solution (100°) of 1 g. of isomer-A (I) (*cis*) in 5 ml. of conc'd acetic acid. Cooling and addition of water gave 0.65 g. (65%) of V; m.p. $147-151^{\circ}$; yellow crystals; recrystallized from methanol; m.p. $151-152^{\circ}$.

Anal. Calc'd for $C_{22}H_{18}N_2O$: C, 81.63; H, 5.36.

Found: C, 81.44; H, 5.18.

This compound was not obtained in a similar experiment on the isomer-B (*trans*).

(*4-Methylphenoxy*)dibenzoyl ethylene-A and -B (*cis* and *trans*) (I and II). The reaction between *dl*-dibenzoyl ethylene dibromide and sodium *para*-cresylate was carried out at -20° according to the procedure for the phenoxy compound (above). Crystallization of the product from butanone gave a first crop (61%) of the isomer-A (*cis*) and concentration gave a second crop (19%) of the new isomer-B (*trans*). The latter, yellow, was recrystallized from methanol; m.p. $99-102^{\circ}$.

Anal. Calc'd for $C_{22}H_{18}O_2$: C, 80.69; H, 5.30.

Found: C, 80.88; H, 5.27.

The *meso* dibromide (IV) did not react under these conditions.

Comparison of the reactions of the dl- and meso-dibenzoyl ethylene dibromides and cis- and trans-chlorodibenzoyl ethylenes with sodium para-cresylate. Reaction in ethanol at 3° for 5 hours, and addition of water gave products which were separated by fractional crystallization from an ethanol-butanone mixture. From the *meso*-isomer the yield of *cis* was 81%. From the *dl*-isomer the yield of *cis* was 67%, and from the filtrate the *trans* isomer was obtained (23%, very crude) and crystallized from absolute ethanol in a yield of 10% (pure). Reaction at 27° gave 85% of the *trans* from the *meso* and 84.5% from the *dl*; in the latter case a small amount of *trans* isomer was isolated and crystallized from absolute ethanol; 55%, m.p. 98–102°. The reactions with III, *cis* and *trans*, at 2–10° according to the above directions gave 80 and 58% respectively of I-A (*cis*) and small amounts of mixtures of the isomers which were not separated.

Conversion of the cis isomer (A) (I) to the trans isomer (B) (II) was accomplished by 6-hours' exposure of a benzene solution to sunlight. Reduction of both isomers-A and B (I and II) to the same saturated diketone (6), was effected as above by sodium hydro-sulfite.

*Oxidation of 2,5-diphenyl-3-(4-methylphenoxy)furan (VI) with conc'd nitric acid, carried out in propionic acid at 0° in the usual way (cf. 16) gave I in 81% yield; identified by recrystallization (m.p. 168–169°) and mixture m.p. The isomer-B (*trans*) (II) under identical conditions was recovered (88%) unchanged.*

SUMMARY

In three cases stereoisomeric aroxydibenzoyl ethylenes are formed in the reaction between sodium aroxide and dibenzoyl ethylene dibromide. The dominant higher-melting isomers, and the several alkoxydibenzoyl ethylenes which are known each only in one form, are assigned *cis* configurations on the basis of the conversion in one case into the pyridazine, the synthesis of several of them from the corresponding furans by oxidative ring cleavage, the consistently larger extinction coefficients of the main ultraviolet absorption bands, and the probable relative interferences of groups as predicted on the basis of planar scale drawings based on van der Waals' radii. The ring-chain tautomerism of hydroxydibenzoyl ethylene and the configurations of the amino- and substituted-amino-dibenzoyl ethylenes are discussed in the light of the ultraviolet absorption spectra.

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