lowed to stand at room temperature for 24 hours. By slow fractional crystallization of the resulting material to produce large crystals, 90% of pure starting material was recovered. Evaporation of the filtrate almost to dryness gave a small sample of nearly pure product (5–10%; m.p. 174–181°) which was crystallized from benzene and isoöctane; m.p. 180–182.5°.

Anal. Calcd. for $C_{22}H_{19}NO_4$: C, 73.11; H, 5.37; OCH_3, 8.59. Found: C, 73.11; H, 5.30; OCH_3, 8.64.

Upon careful examination of the residues from the above reaction no trace of another product could be found.

In an identical experiment utilizing the *cis* isomer Ib only starting material was recovered and no trace of isomerization product could be detected.

Action of Sodium Peroxide on the *cis*- and *trans*-Chalcones (III)[15].—Addition of 0.6 ml. of 2 *N* aqueous sodium hydroxide to a solution of 0.5 g. of *trans*-chalcone III in 6 ml. of methanol produced an emulsion; 0.8 ml. of 15% aqueous hydrogen peroxide was then added; after 1 min. of reaction time the mixture was poured into 50 ml. of water and the crystalline oxide was filtered; yield 0.47 g. (87%), m.p. 75–80°. In another experiment of 2 min. reaction time the oxide crystallized directly within 1.5 min.; yield 93%, m.p. 76–81.5°. With *cis*-chalcone III on 40% of the above scale, after 2 min. reaction time, no oxide precipitated nor was obtained on working up the mixture; after 6 and 15 min. reaction times 68% yields were obtained (m.p. 68–69° and 78–84°, respectively). Identifications were by mixture melting points.

In drawing conclusions from these experiments it has been assumed that the effect of the initial formation of emulsions is negligible (the solubilities of the *cis*- and *trans*-chalcones are very similar in isoöctane and in ethanol). A further experiment was performed to check this point and to exclude the possibility that the case of the *cis*-chalcone might have involved a rate-determining rearrangement of an intermediate and labile stereoisomeric oxide.

To a solution of 0.5 g. of III in 6 ml. of absolute ethanol was added first 1 ml. of 0.6 *N* absolute ethanolic sodium hydroxide and then 0.8 ml. of 15% aqueous hydrogen peroxide, under stirring. After 2 min. of reaction time the still homogeneous solution was poured into 50 ml. of 0.1 *N* hydrochloric acid, and seeded (in the case of the *trans* isomer, with the oxide, and in the case of the *cis*, with starting material). Crystallization occurred and the product was filtered after 10 min. stirring. From the *cis* compound 0.37 g. (75%) was recovered (m.p. 36–40°), and from the *trans* 0.53 g. (98%) of the oxide (m.p. 76–81.5°). Identifications were by mixture melting points.

CHARLOTTESVILLE, VIRGINIA

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

The Conformations of the *cis* and *trans*-Dibenzoylstyrenes

BY CARL R. BAUER[1] AND ROBERT E. LUTZ

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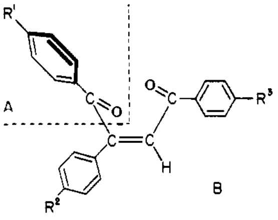
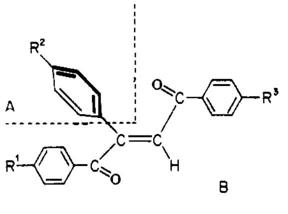
The selectivity of the shift in ultraviolet absorption maxima caused by *p*-monosubstituents, methyl and phenyl, in *cis* and *trans*-dibenzoylstyrenes constitutes supporting evidence for the postulated conformations with respect to effective relative planarities of the principal parts of the conjugated system. The *cis* isomer involves virtually independent *trans*-chalcone and benzoyl systems and the *trans* isomer an effective *trans*-dibenzoylethylene structure. The syntheses of the various compounds employed in these studies, and the proofs of structure and configuration, are described, and in the main followed standard procedures.

Recent studies of molecular models and ultraviolet absorption spectra of *cis*-dibenzoylstyrene (I) indicate that this compound contains two partially independent non-coplanar chromophores, one a *trans*-chalcone (benzalacetophenone) system (B of formula I) which is presumably responsible for the absorption at 302 mμ, and the other a benzoyl group A absorbing at 235 mμ.[2] The *trans* isomer II on the other hand absorbs at 250 mμ. In this isomer there appears to be a typical unsaturated 1,4-diketone system [IIB] which is effectively conjugated throughout and approaches planarity,[2] and an independent non-coplanar phenyl group [IIA] which has little effect on the near ultraviolet absorption and which, although formally so, is actually not effectively conjugated with the vinyl phenyl ketone system. The present investigation was undertaken to substantiate these postulations by identification of the independently effective chromophores by the effect of mono-*p*-substitutions of methyl or phenyl (R^1, R^2 or R^3) which would increase the wave length of absorption of the one chromophore without seriously affecting the other.



I *cis*



II *trans*

R^1, R^2 and R^3 = H except where methyl or phenyl is specified

The lower wave length absorption maximum of *cis*-dibenzoylstyrene at 235 mμ was identified as belonging to the non-coplanar benzoyl group (A of I) by the shift of this band to 265 mμ upon *p*-substitution in this group of a methyl; this substitution failed to change significantly either the position or molar absorptivity of the maximum at 302 mμ attributable to the chalcone structure (B of I) (see Table I). It should be noted, however, that the shift of the lower wave length band is large, 30 mμ, and is comparable to the shift of 12 and 23 mμ caused by insertion of two *p*-methyls into *cis*- and *trans*-dibenzoylethylenes, respectively, and it is to be contrasted with the small bathochromic effect of 8 mμ when *p*-methyls are substituted into dibenzoylethane.

When a *p*-methyl group is substituted in the *cis* isomer on the phenyl at the benzal end of the chalcone system (B of I, $R^2 = CH_3$), one would expect a considerable bathochromic shift of the long wave length absorption maximum, and such an effect is actually observed, namely, 22 mμ, a value

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(1) du Pont Company Postgraduate Fellow, 1949–1950.

(2) (a) L. Kuhn, R. E. Lutz and C. R. Bauer, THIS JOURNAL, **72**, 5058 (1950); (b) *cf.* also, R. E. Lutz and C. R. Bauer, *ibid.*, **73**, 3456 (1951); and (c) R. E. Lutz and R. H. Jordan, *ibid.*, **72**, 4090 (1950); *cf.* a so (d) W. B. Black and R. E. Lutz, *ibid.*, **75**, 5990 (1953).

TABLE I

ULTRAVIOLET ABSORPTION DATA[a]

$R^1C_6H_4COC(C_6H_4R^2)=CHCOC_6H_4R^3$ (R = *p*-); in absolute ethanol as solvent except where otherwise specified[a]

R^1	R^2	R^3	λ_{max}, mμ	$\epsilon \times 10^{-3}$	λ_{min}, mμ	$\epsilon \times 10^{-3}$
cis-Isomers						
H	H	H	235[2]	16.9	...	..
			302	21.0	...	..
CH_3	H	H	265	22.7	300	19.6
			302	19.6	...	..
H[b]	CH_3	H	240	18.4	285	14.6
			324	19.4	...	..
C_6H_5	H	H	295	39.5	...	..
(in isoöctane)			(288)	(39+)	(240)	(9.3)
H	C_6H_5	H	249	23.9	298	14.0
			340	24.3	...	..
H	H	C_6H_5	240	24.4	271	11.5
			325	32.7	...	..
(in isoöctane)			(236)	(24.8)	(265)	(11.0)
			(312)	(34.2)	...	..
trans-Isomers						
H	H	H	258[2]	29.6	...	..
CH_3	H	H	261	22.6	...	..
C_6H_5	H	H	261	20.0	270	21.7
			297	24.9	...	..
(in isoöctane)			(256)	(20.5)	(240)	(18.3)
			(290)	(27.5)	(265)	(18.8)
H	H	C_6H_5	258	20.0	271	16.9
			300	21.8	...	..
(in isoöctane)			(220)	(22.3)	(237)	(18.2)
			(253)	(20.5)	(265)	(18.4)
			(287)	(21.8)	...	..
The saturated diketones						
C_6H_5	H	H	244	17.9	258	14.3
			285	25.8	...	..
H	H	C_6H_5	251	16.5	255	16.4
			283	27.4	...	..
$R^1C_6H_4COCH=CHCOC_6H_4R^2$ (R = *p*-)						
cis; R^1, R^2 = CH_3			272[c]	20.1	225	11.6
(in isoöctane)			(266[c])	(20.6)	(227)	(13.4)
trans; R^1, R^2 = CH_3			230	11.8	238	11.7
			297[d]	17.7	...	..
(in isoöctane)			(225)	(14.0)	(236)	(12.0)
			(285[e])	(19.2)	...	..
Saturated diketone						
R^1, R^2 = CH_3			247.5[f]	36.7	...	..
cis; R^1 = xenyl;			246	14.5	232	14.0
R^2 = H			295	22.4	256	14.2
(in isoöctane)			(288)	(20.8)	(236)	(13.5)
trans; R^1 = xenyl;			261	20.0	227	10.4
R^2 = H			307	17.8	282	15.8
(in isoöctane)			(260)	(22.4)	(226)	(12.7)
			(300)	(19.2)	(280)	(17.2)
cis; R^1, R^2 = xenyl			302[g]	18.2	244	7.0
trans; R^1, R^2 = xenyl			307[h]	26.6	231	13.0
$C_6H_5CH=CHCOC_6H_4C_6H_5$ (*p*-)(*trans*)						
			231	17.7	262	5.7
			320	38.2	...	..
$CH_3COC_6H_4C_6H_5$ (*p*-)						
			282	22.3	...	..

[a] Determined by means of a Beckman DU quartz spectrophotometer, using 0.00005 *M* solutions in absolute ethanol, except when otherwise indicated. Many of the xenyl derivatives were difficultly soluble in isoöctane (2,2,3-trimethylpentane), but some values were obtained in this solvent and are given in parentheses. [b] Sample supplied by Dr. P. S. Bailey [*cf.* P. S. Bailey, E. E. Kawas and L. L. Smith, THIS JOURNAL, **73**, 4088 (1951)]. [c] There were slight shoulders in the absorption curves in the two solvents at 253 mμ (ε 18.5 × 10³) and 268 mμ (ε 15.3 × 10³), respectively. [d] Inflection at 263 mμ (ε 13.8 × 10³) and large shoulder at 252 mμ (ε 13.4 × 10³). [e] There was an inflection at 277 mμ (ε 18.6 × 10³) and broad shoulder at 261 mμ (ε 17.3 × 10³). [f] Slight inflection point at 274–278 mμ (ε 2.2 × 10³). [g] In 0.0000226 *m* solution. [h] In 0.000034 *m* solution. Definite but slight shoulders at 241 mμ and 270 mμ (ε 14.2 and 18.8 × 10³).

very close to that brought about by *p*-substitution in the corresponding phenyl of chalcone itself.[3]

The *p*-substitution of a phenyl[4] in the non-coplanar benzoyl (A of I, $R^1 = C_6H_5$) shifted the characteristic band for this group further than did the *p*-methyl toward the longer wave length (*ca.* 60 mμ), as it was expected to do in view of the effect produced by analogous substitution in acetophenone (see Table I). Although here the wave length of the absorption coincided with that of the chalcone system (B of I), the effect is clearly recognized from the approximately doubled molar absorptivity at this maximum and the absence of an absorption peak in the region 240–260 mμ. As in the case of substitution of a methyl at the non-coplanar benzoyl (A of I, $R^1 = CH_3$), the wave length of the chalcone group absorption was not altered significantly by this comparable substitution of the phenyl.

These above described effects identify the shorter wave length band of the *cis* isomer as that of the partially independent benzoyl (A of I).

p-Substitution of a phenyl at one end or the other of an effective chalcone system should increase the wave length of absorption of that system, and to the greater degree in the isomer in which the unsaturated ketone system has been extended by the conjugation with a β-phenyl (*cf.* B of I where R^2 = phenyl). Such increases in wave length are observed in the *cis* isomer and are of the expected order of magnitude; when R^3 = phenyl, the increase is 20 mμ (ε 32.7 × 10³) as compared with 35 and 42 mμ for substitution of first one and then the second *p*-phenyl in *cis*-dibenzoylethylene; when R^3 = H and R^2 = phenyl, the increase is considerably greater, namely, 35 mμ (ε 24.3) and comparable with that brought about by similar substitution in *trans*-chalcone itself.[3] The results therefore specifically identify the longer wave length chalcone absorption band of the *cis* isomer (B of I).

In the case of *trans*-dibenzoylstyrene (II) where the phenyl (A) is regarded as non-coplanar with the dibenzoylethylene system (B), there is only one main band at 258 mμ. There the substitution of a *p*-phenyl in either of the terminal phenyls (R^1 or $R^3 = C_6H_5$) produces practically the same effect, namely, a shift of the main peaks 40–50 mμ toward the longer wave length, an effect which is similar to that of *p*-substitution of phenyl into acetophenone, dibenzoylethane and the dibenzoylethylenes (see Table I). The long wave length absorption of these new *trans* *p*-phenyldibenzoylstyrene deriva-

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(3) H. H. Szmant and A. J. Basso, *ibid.*, **74**, 4397 (1952).

(4) Biphenyl itself absorbs at 251 mμ (ε 18.5 × 10³). *Cf.* M. Pestemer and E. Mayer-Pitsch, *Monatsh.*, **70**, 104 (1937).

tives are in the region 300 mμ; however, it is noteworthy that absorption peaks in the region 251–261 mμ which are characteristic of the dibenzoylethylene system, appear also in both cases.

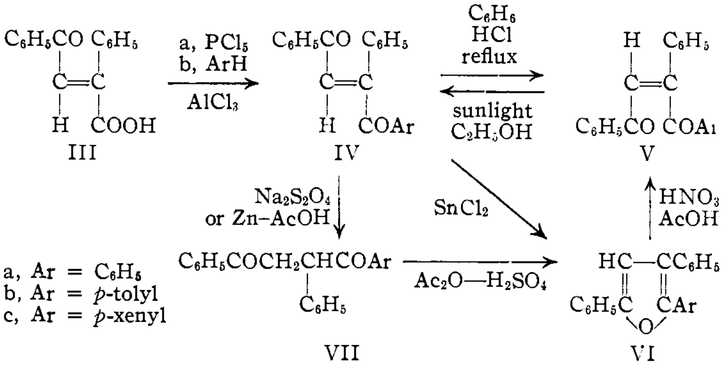
On the other hand, *p*-substitution of a phenyl at the 2-phenyl (R^2) of IIB (in the *trans* compound) would in the absence of steric interference increase the wave length of absorption of the effective chalcone system considerably. No such effect was produced here, and it is therefore clear that the biphenyl group is not effectively conjugated with the rest of the system and is not co-planar with it.

From another viewpoint it should be noted that the doubly-peaked absorption curves of the phenyldibenzoylethanes containing a *p*-phenyl in one or the other of the benzoyl groups, correspond closely with those of the corresponding *trans* unsaturated diketones, and are different in character from those of the *cis* isomers. There is in the case of the *trans* isomers a consistent bathochromic shift of 2 and 17 mμ with respect to the saturated diketones. On the other hand, there is a much wider range of variations in the curves of the *cis* isomers as compared with those of the saturated diketones both with respect to the maxima and the molar absorptivities. The reduction of the *trans* compounds removes only the small amount of extra conjugation provided by the double bond connecting the terminal coplanar benzoyl groups whereas in the *cis* isomer it destroys the conjugation of the chalcone system.

A problem of interest in this field appears upon comparison of the ultraviolet absorption characteristics of the simple *cis*- and *trans*-diaroylethylenes (see Table I). The introduction into the *p*-positions of *cis*-dibenzoylethylene of two methyls, or of either one or two phenyls, shifts the relatively simple and symmetrical absorption peaks toward the longer wave length. However, these same *p*-substitutions in the *trans* isomer produce a more drastic effect. In the cases of the two methyls or of the two phenyls the absorption bands become very broad and unsymmetrical with the greater bathochromic shifts. In the case of substitutions of a phenyl at one end only, however, producing an unsymmetrically substituted molecule, there is observed two actually distinct maxima at wave lengths not far from those expected of independent α,β-unsaturated benzoyl and *p*-xenoyl chromophores. An extension of this study of the unsaturated 1,4-diaroyl system is in progress.

The Syntheses and Proofs of Structure of the Unsaturated 1,4-Diketones.—The labile *trans*-dibenzoylstyrene (IVa) was successfully made by Olivera-Mandalà[5] by the action of sunlight on the *cis* isomer Va. This work has now been verified by another and unequivocal chemical synthesis from the *trans* acid, which has been employed also to make the analogous 1-*p*-tolyl and 1-*p*-xenyl series (IV–VII, b, c). The following chart (III–VII) illustrates the successful group of reactions starting from β-benzoyl-α-phenylacrylic acid (III).[6]

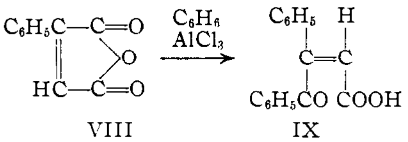
The *trans* acid III was converted by phosphorus pentachloride to the acid chloride which was freed from excess phosphorus oxychloride and used directly in Friedel–Crafts reactions with benzene, toluene and biphenyl. The conclusion that the acid III has the *trans* configuration assigned by Kohler, *et al.*,[6] and that this configuration has been retained in the products IV is supported by the following arguments: (a) if the acid chloride had been *cis* it presumably would not have reacted successfully in its open-chain form in the Friedel–Crafts reaction; (b) the labile (*trans*)-dibenzoylstyrene is obtained and not the stable (*cis*) isomer, and this shows that no catalyzed stereochemical changes have occurred during the reaction; and (c) the *trans* arrangement of the product is demonstrated by the subsequent relationships between it and the *cis* isomer V and the furan VI.



a, Ar = C_6H_5
b, Ar = *p*-tolyl
c, Ar = *p*-xenyl

The labile *trans* unsaturated diketones IV produced by the above syntheses were converted under acid catalysis to the stable *cis* isomers V, and regenerated by the action of sunlight on suitable solutions of the latter. Sodium hydrosulfide reduction of the unsaturated diketones IV gave the saturated diketones VII. The furans VI were obtained either directly by zinc–acetic acid reduction of the unsaturated diketones IV or in two steps by reduction to, and dehydration of, the saturated diketones VII. Nitric acid oxidation of the furans produced the *cis* unsaturated diketones V.

Since the above synthesis of *trans*-dibenzoylstyrene was successful the similar synthesis which had been started through *trans*-β-benzoyl-β-phenylacrylic acid (IX)[7] was not completed, and the experiments in this field (which have taken another direction) will be reported in a later paper. This acid IX was obtained by the Friedel–Crafts re-



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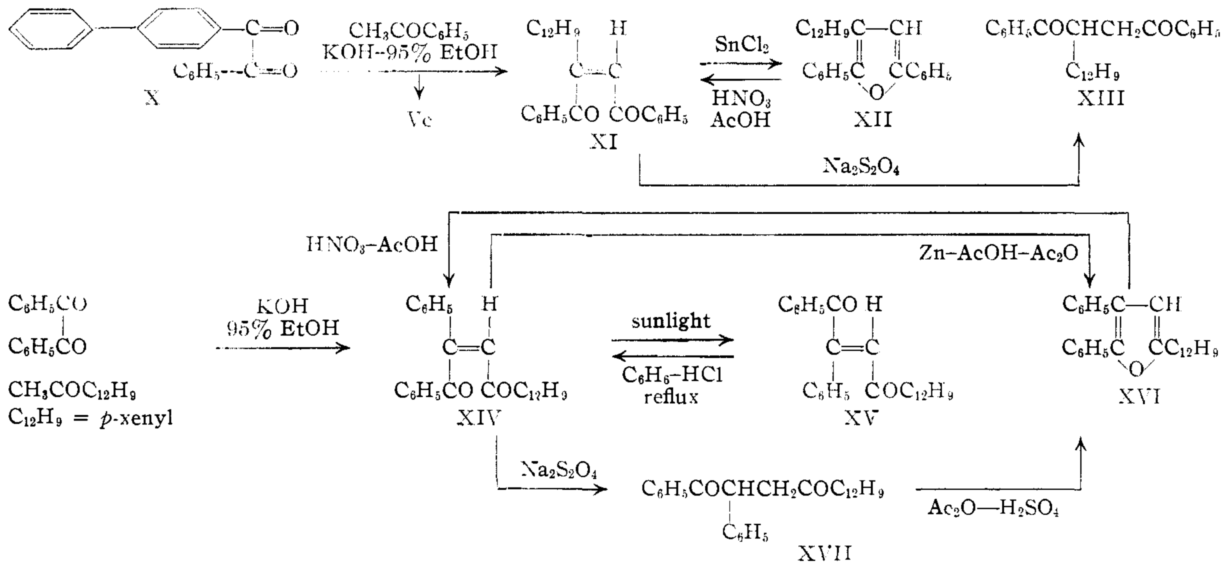
[5] E. Olivera-Mandalà, *Gazz. chim. ital.*, **45**, 138 (1915).

[6] (a) E. P. Kohler, W. D. Peterson and C. L. Bickel, THIS JOURNAL, **56**, 2000 (1934); (b) E. P. Kohler and R. C. Goodwin, *ibid.*, **49**, 226 (1927).

[7] F. R. Japp and W. B. Davidson, *J. Chem. Soc.*, **67**, 132 (1895); (b) F. R. Japp and G. P. Lander, *ibid.*, **71**, 132, 142, 155 (1897); (c) C. L. Reiner, *Ber.*, **14**, 1797 (1881); (d) J. Thiele and F. Straus, *Ann.*, **319**, 174 (1901).



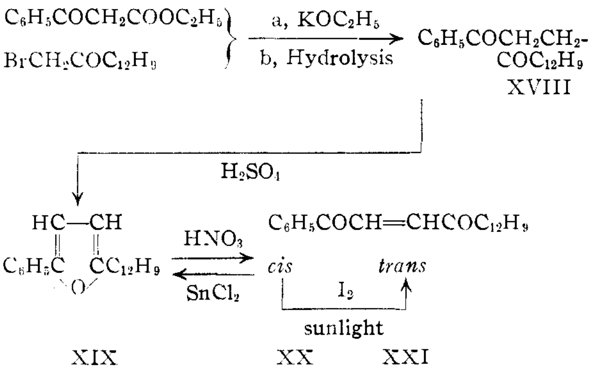
action upon phenylmaleic anhydride (VIII), a new synthesis which establishes its configuration.

The seemingly logical synthetic approach through the Friedel–Crafts reaction between benzene and the diacid chloride of phenylfumaric acid, a type of reaction which has proved to be generally successful in the field, was begun but was also abandoned. In this case several unsuccessful attempts to make phenylfumaric acid led us to question the literature report of the existence of this acid[8] and to conclude that the supposed "phenylfumaric acid" of Almstrom[8a] was really phenylmaleic acid. It is possible that phenylfumaric acid, which would at the same time be β-carboxy-*trans*-cinnamic acid, may, like *trans*-dibenzoylstyrene, be the labile form[9]; molecular models are in accord with this view, and a study of this problem is in progress.

The synthesis of the isomeric types of unsaturated 1,4-diketones carrying the *p*-xenyl group in the 2-position or the 4-position on the chain (XI–XIII and XIV–XVII), began with the base-catalyzed condensation of benzil or phenyl xenyl diketone (X) with acetophenone or with methyl xenyl ketone, following the method employed by Allen and Hubbard[10] for the preparation of the parent *cis*-dibenzoylstyrene itself and the 4-*p*-xenyl analog XIV. Two products were obtained when the unsymmetrical phenyl xenyl diketone (X) was used, namely, XI and Vc. Structural assignments follow from the independent and unequivocal synthesis of one of these two diketones Vc from *trans*-β-benzoyl-α-phenylacrylic acid (III).

The α-diketone condensations in all cases studied produced the stable *cis* unsaturated 1,4-diketones; the configurations follow from the cycle of reactions, direct reduction or reduction through the saturated diketones (XIII, XVII) to the furans (XII, XVI), and nitric–acetic acid oxidative fission of the furans to regenerate these same (stable) *cis* unsaturated diketones (XI, XIV). In one case of these two XIV the labile *trans* isomer XV was prepared by sunlight inversion.

The parent 1,4-diketones with no chain substituents and with one *p*-xenoyl group were made for comparative purposes using the Kapf and Paal synthesis[11] involving the condensation of benzoylacetic ester and bromomethyl *p*-xenyl ketone, decarboxylation to the saturated diketone XVIII, followed by furanization to XIX, nitric–acetic acid oxidation to the, in this case, labile *cis* unsaturated diketone XX, and inversion to the stable *trans* isomer XXI.



The *cis*-di-(4-xenoyl)-ethylene (new) together with the known *trans* isomer were also made by standard procedures.

Experimental[12]

Phenylmaleic Anhydride and Acid. Attempted Preparation of Phenylfumaric Acid.—In a number of experiments material corresponding in preparation and properties to Almström's "Phenylfumaric acid"[8a] was treated with phosphorus pentachloride and in each case the recovered solid was proved to be phenylmaleic anhydride.[6a] This and the

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[8] (a) G. K. Almstrom, *Ber.*, **48**, 2009 (1915); (b) H. Alexander, *Ann.*, **258**, 67 (1890).

[9] For work dealing with the stabilities and ultraviolet absorptions of the *cis*- and *trans*-cinnamic acids, see: A. Smakula and A. Wassermann, *Z. physik. Chem.*, **A155**, 353 (1931); E. Havinga and R. J. F. Nivard, *Rec. trav. chim.*, **67**, 846 (1948); P. Ramart-Lucas, *Bull. soc. chim.*, **9**, 868 (1942).

[10] C. F. H. Allen and J. R. Hubbard, THIS JOURNAL, **52**, 384 (1930); (*cf.* also ref. 7).

[11] S. Kapf and C. Paal, *Ber.*, **21**, 1485, 3056 (1888).

[12] (a) Melting points are "corrected"; (b) many of the microanalyses were by Mrs. Anne Wilgus, and a few were by Miss Patricia L. Paynter; (c) a few of the experiments were carried out in this Laboratory by Dr. Chi-Kang Dien, Post-doctorate fellow, under a project supported by a grant from the Office of Ordnance Research.

further experiments below led us to the conclusion that Almström's preparation involved merely hydration of phenylmaleic anhydride to phenylmaleic acid and that phenylfumaric acid has not yet been isolated.

A suspension of 0.4 g. of phenylmaleic anhydride in 3 ml. of water was allowed to stand for 2 days during which time solution became completed. Extraction by ether, evaporation, solution of the residue in the minimum amount of cold ethanol and precipitation by addition of dry benzene gave a product of m.p. 125–127° which appeared to be identical with the product "phenylfumaric acid" of m.p. 126–128° prepared by Almström's method. In similar experiments Alexander[8b] apparently isolated the same compound (but melting unsharply at 100°) which corresponded in analysis to phenylmaleic acid. The various samples undergo decomposition at the melting points to give phenylmaleic anhydride. It is clear that these various products are phenylmaleic acid. The melting point given by Alexander for his material represents a discrepancy which, if not an error, is probably not serious in view of the nature of this compound.

In another experiment an aqueous solution of phenylmaleic anhydride which had been carefully neutralized with sodium hydroxide was heated at 190–210° in a sealed tube for 100 hours (*cf.* the method of preparation of dimethylfumaric acid from dimethylmaleic anhydride[13]). Only phenylmaleic acid was recovered.

cis-**β-Benzoyl-β-phenylacrylic Acid (IX)** (*cf.* 6).—A solution of 7 g. (0.04 mole) of phenylmaleic anhydride (VIII) in 25 ml. of dry benzene was added over 25 min. to a stirred suspension of 12 g. (0.09 mole) of anhydrous aluminum chloride in 60 ml. of benzene. After stirring for another half-hour the deep red reaction mixture was hydrolyzed in ice and concd. hydrochloric acid. The benzene solution after washing was concentrated; dilution with isoöctane gave 5 g. (50%) which was recrystallized from benzene, m.p. 140–141°.

Anal. Calcd. for $C_{16}H_{12}O_3$: C, 76.17; H, 4.80. Found: C, 76.33; H, 5.03.

trans-**1,2-Dibenzoylstyrene (II, IVa)**.—A mixture of 1.5 g. (0.006 mole) of *trans*-β-benzoyl-α-phenylacrylic acid (III)[6] and 1.25 g. (0.006 mole) of phosphorus pentachloride was triturated and after reaction was complete the phosphorus oxychloride was evaporated under reduced pressure at room temperature. The crude residual acid chloride was dissolved in 20 ml. of benzene and added slowly to a well-stirred mixture of 2 g. of anhydrous aluminum chloride and 20 ml. of benzene. After stirring for a half-hour at room temperature, hydrolysis gave 0.85 g. (46%) of II which after crystallization from ethanol melted at 126°.

trans-**2,4-Diphenyl-1-(4-tolyl)-2-butene-1,4-dione (IVb)** was prepared by the above type of Friedel–Crafts reaction using toluene at 45° and standing for 10 min. after addition of the acid chloride of III to the reaction mixture.

Anal. Calcd. for $C_{23}H_{18}O_2$: C, 84.61; H, 5.56. Found: C, 84.15; H, 5.46.

trans-**2,4-Diphenyl-1-(4-xenyl)-2-butene-1,4-dione (IVc)**.—A solution of the crude acid chloride from 1.5 g. of III in 30 ml. of carbon disulfide was added to a suspension of 3 g. of anhydrous aluminum chloride in a solution of 3 g. of biphenyl in 20 ml. of carbon disulfide. The reaction mixture was stirred for 30 min. and worked up in the usual way. The product was recrystallized from an ethanol–benzene mixture; yield 39%, m.p. 123–124°.

Anal. Calcd. for $C_{28}H_{20}O_2$: C, 86.59; H, 5.19. Found: C, 86.58; H, 5.47.

cis-**1,4-Diphenyl-2-(4-xenyl)-2-butene-1,4-dione (XI)**.—A solution of 1.0 g. of potassium hydroxide in 17 ml. of 90% ethanol was added to a mechanically stirred solution of 6.0 g. (0.02 mole) of 4-phenylbenzil (X)[14] and 3.5 g. (0.03 mole) of acetophenone in 50 ml. of absolute ethanol at 40°. The mixture was held at 40° for 15 minutes and then heated to refluxing for 2 minutes.

The mixed products were precipitated with excess water and the desired diketone was isolated as the first precipitate upon crystallization from hot ethanol containing some benzene. After several recrystallizations from ethanol–benzene mixture it melted at 198°.

Anal. Calcd. for $C_{28}H_{20}O_2$: C, 86.59; H, 5.19. Found: C, 86.28, 86.44; H, 4.86, 5.52.

Upon addition of water to the filtrate from the above separation a small amount of the *cis*-1-(4-xenyl) isomer Vc was isolated and identified by mixture melting point with a sample made from III.

The above *cis* compound XI was also obtained by the nitric acetic acid oxidation of the furan XII by the procedure described below, and identified by mixture melting point.

cis-**1-Phenyl-4-(4-xenyl)-butane-1,4-dione (XVIII)**.—Following the method of Kapf and Paal,[11] 7 g. (0.036 mole) of benzoyl ethylacetate was added to a solution of 0.83 g. (0.036 mole) of sodium in 200 ml. of absolute ethanol under stirring and reflux, and after a few minutes 10 g. (0.036 mole) of bromomethyl 4-xenyl ketone was added. Refluxing for 15 min., decanting from sodium bromide, evaporation to 30 ml. and chilling, gave a crystalline deposit, 11 g. (78%), of crude 2-carbethoxy-1-phenyl-4-(4-xenyl)-butane-1,4-dione, $C_6H_5COCH(COOC_2H_5)CH_2COC_{12}H_9$. This was hydrolyzed by adding a portion (1 g.) to 75 ml. of water, 20 ml. of triethylamine and enough ethanol to effect solution. Refluxing for 3 hours, cooling and recrystallizing the precipitate from ethanol–benzene mixture gave 0.5 g. (62%); m.p. after further crystallizations, 188°.

Anal. Calcd. for $C_{22}H_{18}O_2$: C, 84.03; H, 5.77. Found: C, 84.24; H, 6.00.

Reductive Furanizations of the Unsaturated 1,4-Diketones. 3,5-Diphenyl-2-(4-tolyl)-furan (VIb).—In a typical preparation 0.21 g. of the diketone (IVb) was added to a refluxing solution of 1 g. of stannous chloride in a mixture of 2 ml. of concd. hyrochloric acid and 6 ml. of concd. acetic acid, and refluxing was continued for 15 min. The mixture was poured into water and the resulting precipitate was recrystallized from an ethanol–benzene mixture; yield 0.17 g. (86%), m.p. 119–120°.

Anal. Calcd. for $C_{23}H_{18}O$: C, 88.96; H, 5.84. Found: C, 88.63; H, 5.78.

3,5-Diphenyl-2-(4-xenyl)-furan (VIc) was prepared and purified as above using a 3:5 ml. ratio of concd. hydrochloric and acetic acids, m.p. 135–136°.

Anal. Calcd. for $C_{28}H_{20}O$: C, 90.31; H, 5.41. Found: C, 90.36; H, 5.85.

2,5-Diphenyl-3-(4-xenyl)-furan (XII) was prepared using a 1:1 ml. ratio of concd. hydrochloric and acetic acids; it was purified as above; m.p. 124°, yield 51%.

Anal. Calcd. for $C_{28}H_{20}O$: C, 90.31; H, 5.41. Found: C, 90.60; H, 5.72.

2,3-Diphenyl-5-(4-xenyl)-furan (XVI).—A mixture of 3 g. of the *cis* unsaturated diketone XIV, 60 ml. of concd. acetic acid and 5 g. of zinc dust was refluxed for 10 minutes; 3 ml. of acetic anhydride was added and refluxing was continued for 4 min. Filtering and cooling gave 2 g. (70%) of the furan, which after repeated crystallization from ethanol–benzene mixtures melted at 158°.

Anal. Calcd. for $C_{28}H_{20}O$: C, 90.31; H, 5.41. Found: C, 90.10; H, 5.28.

Nitric and Acetic Acid Oxidation of Furans.[15] *cis*-**2,4-Diphenyl-1-(4-tolyl)-2-butene-1,4-dione (Vb)**.—To the solution of 0.09 g. (0.0003 mole) of the furan (VIb) in 3 ml. of concd. acetic acid was added 0.03 ml. of concd. nitric acid. After a few minutes the reacted mixture was poured into water. The product was recrystallized from ethanol, yield 0.065 g. (70%), m.p. 127°.

Anal. Calcd. for $C_{23}H_{18}O_2$: C, 84.61; H, 5.56. Found: C, 84.60; H, 5.84.

cis-**2,4-Diphenyl-1-(4-xenyl)-2-butene-1,4-dione (Vc)**, obtained as above, was recrystallized from ethanol–benzene mixtures, m.p. 151–153°.

Anal. Calcd. for $C_{28}H_{20}O_2$: C, 86.59; H, 5.19. Found: C, 86.64; H, 5.41.

cis-**1,2-Diphenyl-4-(4-xenyl)-2-butene-1,4-dione (XIV)** was made both from condensation of benzil and acetophenone by the method of Allen and Hubbard[10] and by the above oxidative cleavage of the furan XVI; the samples were identified by mixture melting points.

cis-**1-Phenyl-4-(4-xenyl)-2-butene-1,4-dione (XX)** was prepared from the corresponding furan XIX by the proce-

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(13) E. Ott, *Ber.*, **61**, 2124 (1928); R. E. Lutz and R. J. Taylor, THIS JOURNAL, **55**, 1585 (1933).

(14) M. Gomberg and F. J. van Natta, *ibid.*, **51**, 2238 (1929).

(15) *Cf.* R. E. Lutz and F. N. Wilder, *ibid.*, **56**, 978 (1934).

dure for *cis*-dibenzoylethylene, in 42% yield, recrystallized from ethanol–benzene mixture, m.p. 175.5°, colorless.

Anal. Calcd. for $C_{22}H_{16}O_2$: C, 84.59; H, 5.17. Found: C, 84.59; H, 5.40.

Reductions of the Unsaturated to the Saturated Diketones. 1,2-Diphenyl-4-(4-xenyl)-2-butane-1,4-dione (XVII).—A solution of sodium hydrosulfite (0.9 g.) in 4 ml. of water was added to a refluxing solution of 0.5 g. of the unsaturated diketone XIV in 40 ml. of absolute ethanol. After continued refluxing for 45 min. the product was precipitated by adding water and crystallized from ethanol, yield 80%, m.p. 132.5°.

Anal. Calcd. for $C_{28}H_{22}O_2$: C, 86.11; H, 5.68. Found: C, 86.04; H, 6.01.

Dehydration (as below) by acetic anhydride and sulfuric acid gave the furan XVI which was identified by mixture melting point.

2,4-Diphenyl-1-(4-xenyl)-butane-1,4-dione (VIIc) was obtained from IVc by the above procedure in 95% yield, recrystallized from acetic acid–xylene mixture, m.p. 200°.

Anal. Calcd. for $C_{28}H_{22}O_2$: C, 86.11; H, 5.68. Found: C, 86.38; H, 5.92.

This compound, VIIc, was obtained also by zinc–acetic acid reduction (refluxing for 2 min.). Furanization was effected by the procedure below.

Dehydration of Saturated 1,4-Diketones. 2-Phenyl-5-(4-xenyl)-furan (XIX).—In a typical experiment a solution of 0.09 g. of XVIII in a few ml. of acetic anhydride was treated with 1 ml. of acetic anhydride containing 0.001 ml. of concd. sulfuric acid. Reaction was immediate. Hydrolysis with water gave 0.7 g. (85%); recrystallizations from ethanol containing some benzene brought the melting point to 164°.

Anal. Calcd. for $C_{22}H_{16}O$: C, 89.16; H, 5.44. Found: C, 89.36; H, 5.69.

This compound was made also by stannous chloride reduction of the *cis* unsaturated 1,4-diketone XX by the method described above for VIb.

Sunlight Inversions from *cis* to *trans*. *trans*-1,2-Diphenyl-4-(4-xenyl)-2-butene-1,4-dione (IVc).—After sunlight irradiation for 3 days of a solution of 5 g. of Vc (labile) in 70 ml. of acetone and evaporation, the products were dissolved in hot ethanol. From the first crystalline precipitate IVc (the stable isomer) was isolated and purified by recrystallization from ethanol, yield 1 g. (20%), m.p. 107–108°.

Anal. Calcd. for $C_{28}H_{20}O_2$: C, 86.59; H, 5.19. Found: C, 86.54; H, 5.23.

***trans*-1-Phenyl-4-(4-xenyl)-2-butene-1,4-dione [1-Benzoyl-2-(4-xenoyl)-ethylene] (XXI).**[12c]—A solution was prepared by exposure of the labile *cis* isomer XX in chloroform containing enough iodine to maintain color, to strong sunlight for 6 hours. Crystallization of the yellow product from 1:2 benzene–ethanol mixture gave 80% yield, m.p. 158–159°.

Anal. Calcd. for $C_{22}H_{16}O_2$: C, 84.59; H, 5.17. Found: C, 84.51; H, 5.17.

Limited efforts to prepare this compound by the Friedel–Crafts reaction on β-benzoylacrylyl chloride[16] were not successful.

***cis*-1,4-Di-(4-xenyl)-2-butene-1,4-dione [1,2-Di-(4-xenoyl)-ethylene].**[12c]—A solution of the stable *trans* isomer[17] in chloroform was exposed to strong sunlight for 7 hours, colorless, crystallized from 3:1 benzene–ethanol mixture, m.p. 239–241°.

Anal. Calcd. for $C_{28}H_{20}O_2$: C, 86.57; H, 5.19. Found: C, 86.22; H, 5.11.

Acid-catalyzed inversions from *trans* to *cis* of IVa, b, c and XV were accomplished in 72–90% yields by refluxing for a short time solutions of the compounds in benzene containing a small amount of added concd. hydrochloric acid. The products (Va, b, c and XIV), isolated by washing with water, drying and evaporating, were purified and identified by mixture melting points with samples prepared directly from III.

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(16) R. E. Lutz, THIS JOURNAL, **52**, 3423 (1930).

(17) H. G. Oddy, *ibid.*, **45**, 2160 (1923).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND THE DEFENSE RESEARCH LABORATORY, THE UNIVERSITY OF TEXAS]

Allylic Chlorides. XX. Preparation and Properties of the 1-Bromo-3-chloro-1-propenes[1]

BY LEWIS F. HATCH AND KENNETH E. HARWELL

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The following compounds have been prepared and characterized: *cis*- and *trans*-1,3-dibromopropene, *cis*- and *trans*-3-bromo-2-propen-1-ol and *cis*- and *trans*-1-bromo-3-chloro-1-propene. The bromochloropropenes isomerized at room temperature in the presence of light but did not isomerize in the dark at 0°. The relative reactivities of the allylic chlorides were determined with potassium iodide and with sodium ethoxide. The behavior of these geometrical isomers toward these reagents was similar to that of the 1,3-dichloropropenes.

Recent work with several pairs of geometrical isomers of the type $CHCl{=}CYCH_2Cl$ has shown that the rate of reaction of the allylic chlorine atom with potassium iodide is greater when the vinyl chlorine atom and the chloromethyl group are in the *cis* position in respect to one another.[2] This relationship between reactivity and configuration has been suggested as a means of assigning structure to compounds of this type. The present study of the 1-bromo-3-chloro-1-propenes was undertaken to determine if the same relationship held when the vinyl halogen atom was bromine. These isomers would also further the study of the influence of size and electron attracting power of atoms in this position on the reactivity of the allylic chlorine atom.

The 1-bromo-3-chloro-1-propenes were prepared from 1-bromo-1-propene by treatment with N-bromosuccinimide to obtain 1,3-dibromopropene which was then hydrolyzed to 3-bromo-2-propen-1-ol. The bromoalcohol was converted to 1-bromo-3-chloro-1-propene by concentrated hydrochloric acid.

The 1-bromo-1-propene used was a mixture containing 70% *cis*- and 30% *trans*-1-bromo-1-propene. The 1-bromo-1-propenes isomerize to an equilibrium mixture at room temperature after simple distillation. This isomerization has been noted previously,[3] and it is suggested that most work reported in the literature to have been with either

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(1) For number XIX of this series see L. F. Hatch and G. E. Journeay, THIS JOURNAL, **75**, 3712 (1953).

(2) L. F. Hatch and D. W. McDonald, *ibid.*, **74**, 2911 (1952).

(3) G. Chavanne, *Compt. rend.*, **158**, 1698 (1914).