would provide the best possibility for the formation of an ortho acid because of the strong inductive effect of the fluorine atoms and because of the analogy with the fluoroketones and esters. Trifluoroacetic, pentafluoropropionic and heptafluorobutyric acids form azeotropes with water,[22] the first two having a composition approximating one mole of acid and one mole of water. Infrared spectra of these acids in di-*n*-butyl ether solution and of a mixture of these acids and a molar equivalent of water in di-*n*-butyl ether solution produced the following results: (1) a 15% diminution in the carbonyl absorption upon the addition of water; (2) no carbonyl absorption due to a dimeric product or perfluorocarboxylate ion either before or after the addition of water. It can only be concluded that the 15% diminution in the carbonyl absorption is due either to ortho acid formation or more probably to a solvent effect due to hydrogen-bonding.

Amides.—Sodium methoxide adds to trifluoroacetamide in di-*n*-butyl ether solution forming an addition compound, $CF_3C(OC_2H_5)(NH_2)O^-Na^+$. The addition in this reaction is about 50% complete, much less than that of the corresponding ester. This decrease may be due to comparatively greater ability of nitrogen to reduce the electrophilic character of the carbonyl carbon atom.

Conclusions

The transesterification reaction has been shown to follow the same pattern as ester hydrolysis with regard to kinetics, type of fission and effect of structure.[23] Addition compounds should then be expected as intermediates in the transesterification reaction as well as in ester hydrolysis,[1] and all the foregoing compounds with the general formula $RC(OR)_2O^-Na^+$ can be considered to be examples of stable intermediates in base-catalyzed transesterification.

The striking increase in percentage addition of sodium alkoxide in the series ethyl acetate, ethyl fluoroacetate, ethyl difluoroacetate and ethyl trifluoroacetate—each an equilibrium process—parallels an enormous increase in the rates of alkaline hydrolysis in the series, ethyl acetate, ethyl chloroacetate, ethyl dichloroacetate and ethyl trichloroacetate.[24] The parallel effect of structure on the addition equilibria and the rates of hydrolysis indicates that the slow step in the alkaline hydrolysis of esters may be the addition of hydroxide ion to the carbonyl carbon. It was mentioned previously that the hydrolysis intermediate $RC(OR)(OH)O^-Na^+$ is not stable because of its seeming instantaneous decomposition to carboxylate ion. This again suggests that in the basic hydrolysis of an ester the slow step is the addition of an hydroxide ion to the ester, which is then followed by a fast decomposition to carboxylate ion.

The addition compound $RC(OR)(NH_2)O^-Na^+$ may be a stable prototype of the intermediate in the amination of esters or in the reverse reaction.

Acknowledgment.—The author wishes to express his thanks to Dr. F. H. Westheimer and Dr. E. Rapkin for discussion about various phases of this work and to Dr. E. R. Lippincott and Dr. R. B. Bernstein for advice and assistance with the infrared spectra.

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[22] D. R. Husted and A. H. Ahlbrecht, THIS JOURNAL, **75**, 1605 (1953).

[23] R. W. Taft, Jr., M. S. Newman and F. H. Verhoek, *ibid.*, **72**, 4511 (1950).

[24] D. Flom, Ph.D. Thesis, Pennsylvania State College, 1952. Unpublished results of D. Flom and of this Laboratory indicate a similar increase in the rates of alkaline-hydrolysis of the fluorinated esters.

CHICAGO 16, ILLINOIS

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

Evidence for the *cis–trans* Configurations and Effective Conjugations of α-Phenylchalcones

BY W. BRUCE BLACK[1] AND ROBERT E. LUTZ

RECEIVED APRIL 27, 1953

Determination and interpretation of the ultraviolet absorptivities of the *cis*- and *trans*-α-phenylchalcones and of their 2-(4-nitro) and 3-(4-nitro) derivatives have demonstrated the configurations and conformations of the isomers. The conclusion has been drawn that the *cis* isomers involve effective conjugation of the *trans*-stilbene system only, whereas the *trans* isomers involve effective contributions of both the *cis*-stilbene and *trans*-chalcone conjugations. The greater reactivity of the *trans* isomers toward nucleophilic 1,4-additions has been demonstrated and is consistent with and supports this conclusion.

This investigation is a part of a broader study of stereoisomeric pairs of chalcones (benzalacetophenones) (*cf.* III, Fig. 1) carrying α, β, or α,β-di-substituents,[2] which deals particularly with the important differences in ultraviolet absorptions exhibited by each of a *cis–trans* pair, and also the difference shown by α- and β-structural isomers of either the *cis*- or the *trans*-chalcone molecule, differences which should be (and are) in some degree a measure of the steric and electronic effects of the substituent, and of the effectiveness and reactivities of the conjugated systems present. The work stemmed from a restudy of Stobbe's supposed three isomers of α-phenyl-(4-nitrobenzal)-acetophenone[3a] (Ib, IIb), in which we have been able to find evidence for only two isomers.[3b]

The configurations of the three *cis–trans* pairs under study, the α-phenylchalcones and two of the three possible pairs of mono-(*p*-nitro) derivatives, are shown in formulas I and II. The spectra of

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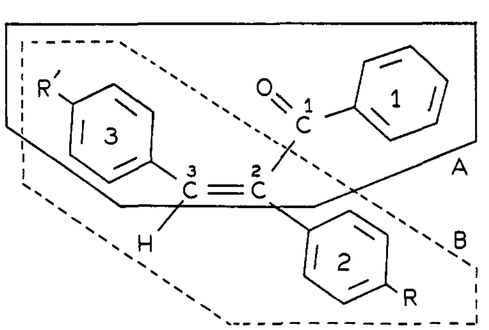
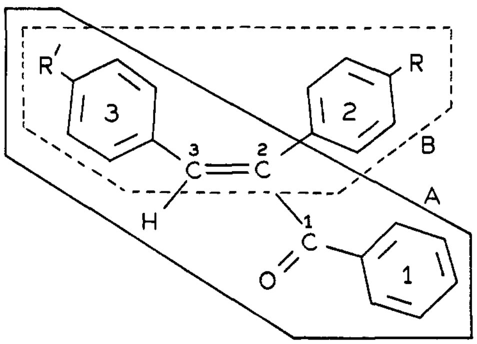
[1] Philip Francis du Pont Fellow, 1952–1953.

[2] (a) R. E. Lutz and R. H. Jordan, THIS JOURNAL, **72**, 4090 (1950); (b) L. P. Kuhn, R. E. Lutz and C. R. Bauer, *ibid.*, **72**, 5058 (1950); (c) R. E. Lutz, D. F. Hinkley and R. H. Jordan, *ibid.*, **73**, 4647 (1951).

[3] (a) H. Stobbe and F. J. Wilson, *Ann.*, **374**, 237 (1910); (b) W. B. Black and R. E. Lutz, THIS JOURNAL, **75**, 4578 (1953).



I, *cis*-α-phenylchalcone (*trans*-benzoylstilbene): (a) m.p. 88–89°; (b) m.p. 168–169.5°; (c) m.p. 135.5–136°



II, *trans*-α-phenylchalcone (*cis*-benzoylstilbene): (a) m.p. 103–103.5°; (b) 153–153.5°; (c) m.p. 188–189.5°

(The phenyl groups are numbered in terms of position on the propenone chain; A, chalcone system; B, stilbene system), (a) R = H, R' = H; (b) R = H, R' = NO_2; (c) R = NO_2, R' = H.

these compounds, involving in each case two maxima, served as the basis for the assignment of the configurations; these spectra are shown in Figs. 1–5 which include also the absorption curves of the reference compounds, the parent *cis*- and *trans*-chalcones and stilbenes themselves. Since the *cis*- and *trans*-α-phenylchalcones are at the same time substituted *trans*- and *cis*-stilbenes, respectively, it should be emphasized that the arbitrarily chosen structural standard of reference is the chalcone system, and that the equally important reference to these same compounds as stilbenes will be parenthetical.

***cis*-4-Nitrochalcone** (*cf.* IV, Fig. 1) (new) was made and studied in order to make certain that, as in the case of the *trans* isomer,[4] the substitution of the nitro group did not cause a significant bathochromic shift in absorption in the 300 mμ region. It was prepared by sunlight or sunlamp exposure of solutions of the *trans* isomer. Photoequilibrium was established within a few hours [within a few minutes at 10^{-5} *M* concentrations] and involved a ratio of *cis* to *trans* of 72:28 (±5)%. The molar

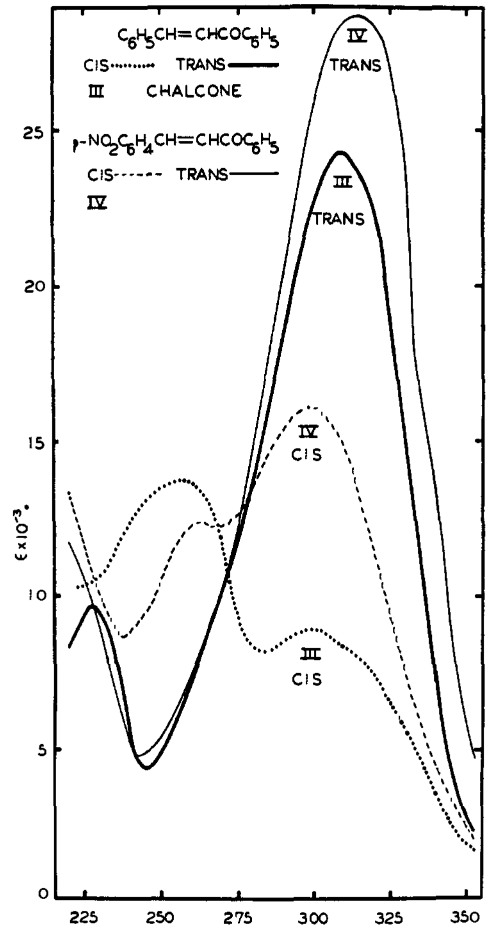


Fig. 1.—Absorption spectra of the *cis*- and *trans*-chalcones (III) and the *p*-nitro derivatives IV.

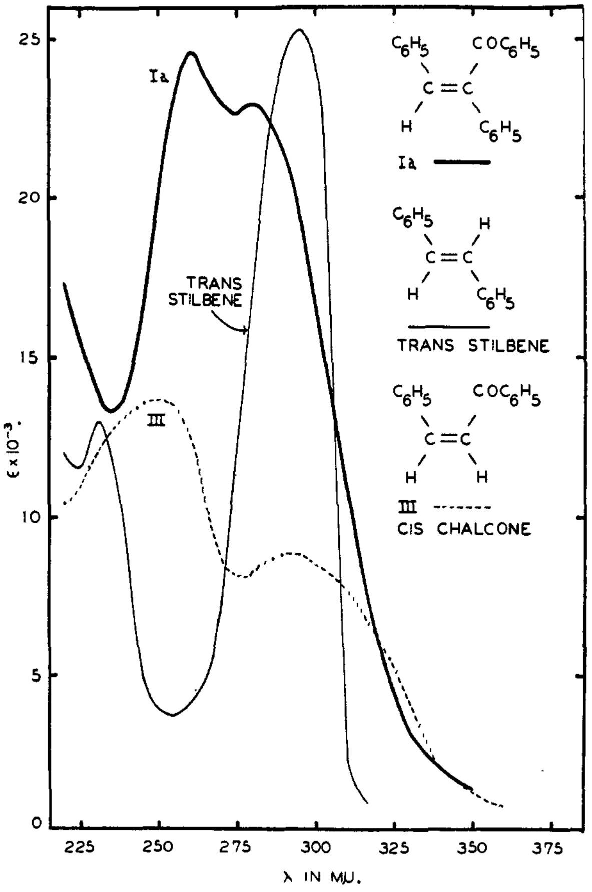


Fig. 2.—Absorption spectrum of *cis*-α-phenylchalcone (Ia).

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[4] (a) V. Alexa, *Bul. Soc. Chim. România*, **18A**, 93 (1936); **1**, 77 (1939). *Cf.* also (b) H. H. Szmant and A. J. Basso, THIS JOURNAL, **74**, 4397 (1952).

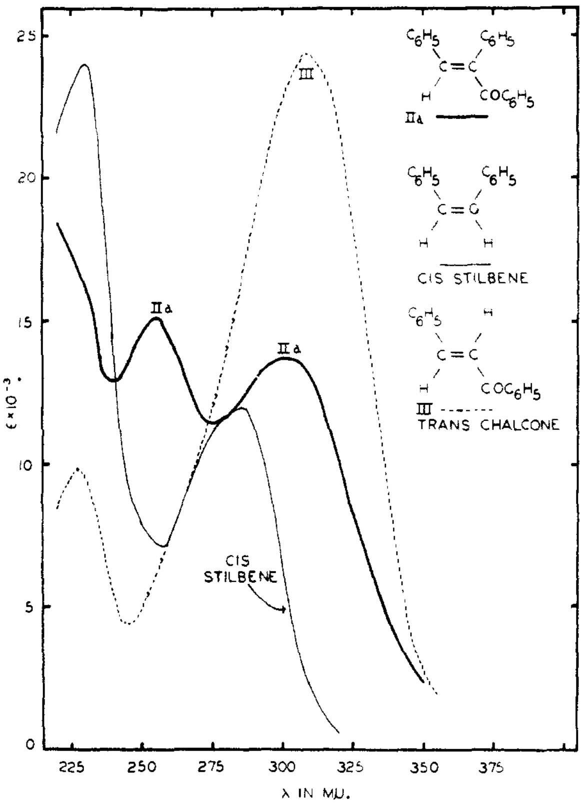

Fig. 3.—Absorption spectrum of *trans*-α-phenylchalcone (IIa).

absorptivity at the longer wave length maximum decreases very considerably in going from the *trans* to the *cis* isomer (28 to 16×10^3) while there developed a strong absorption maximum in the 260 mμ region (Fig. 1). This type of change is typical of *cis*- and *trans*-chalcones themselves[2a] and the α-bromo derivatives.[2c] As the degree of planarity of the principal conjugated system decreases in going from *trans* to *cis*, the molar absorptivity at the long wave length becomes less and the absorptivity in the region 240–260 mμ characteristic of an independently functioning benzoyl group increases.[5]

It should be noted that substitution of the *p*-nitro group in the 3-phenyl of *cis*-chalcone (III to IV) sharply raises the molar absorptivity of the longer wave length band and lowers it slightly in the shorter wave length band. In the *trans* isomer there is a similar but smaller increase in molar absorptivity at the single long wave length maximum.

Comparison of the absorption of *cis* and *trans* α-phenylchalcones with those of the 3-(4-nitro) derivatives (Fig. 2–5) led to three observations: (1) The *p*-substitution of a nitro group in the 3-phenyl group in *cis*- and *trans*-α-phenylchalcones brought about marked bathochromic shifts in the maxima of the longer wave length peaks, namely, 47.5 and 18.5 mμ, respectively.[6]

(2) In both of the above stereoisomeric pairs (Ia–IIa and Ib–IIb) one isomer had considerably higher molar absorptivities than did the other for both the shorter and the longer wave length bands.

(3) The values of the molar absorptivities of the shorter wave length maxima in the 240–250 mμ region in both the *cis*-α-phenylchalcone and its 3-(4-nitro) derivative (Ia, Ib) are extraordinarily high, too high even to be accounted for by the effect of an isolated benzoyl group which normally involves a molar absorptivity of about 14×10^3; whereas the molar absorptivities of the longer wave length maxima are of the order expected of a *trans*-chalcone system for which the absorption corresponding in wave length to that of a benzoyl group would be lower rather than higher.[2] This effect is more apparent in the 3-(4-nitro) compound Ib in which the introduction of the nitro group in the 3-phenyl causes a separation of the two maxima sufficient for independent evaluation, than it is in the parent *cis*-α-phenylchalcone itself (Ia) where a part of the height of the shorter wave length peak is caused by the effect of overlapping of this and the longer wave length peak.

Discussion of Observation (1) and Assignment of *cis*-Chalcone (*trans*-Stilbene) Configurations.—The large bathochromic shifts of the long wave length bands must necessarily be due primarily to the nitro group acting in conjugation with the stilbene system rather than with the chalcone system. This conclusion is supported by the fact that *p*-nitro substitution in the benzal group of the parent chalcones themselves produces a bathochromic shift of only 5 mμ in the *cis* isomer and 8 mμ in the *trans*,[4] whereas *p*-nitro substitution in *cis*- and *trans*-stilbenes produces comparatively large bathochromic shifts of 44 and 55 mμ, respectively.[7] Since the shift observed specifically in the case of the 3-(4-nitro) compound Ib as compared with Ia (47.5 mμ) is of the same order of magnitude as that produced by the *p*-substitution of a nitro in the *cis*- or *trans*-stilbenes, the longer wave length maximum must here be due to a predominantly effective stilbene conjugation.[8]

That the stilbene systems of these isomers (Ia and Ib) are actually *trans* is supported by the self-consistency of the following points: (a) the shift in the longer wave length maximum of 47.5 mμ caused by *p*-substitution of a nitro in the 3-phenyl group is of the expected order for substitution in a *trans*-stilbene and is actually greater than that caused by *p*-substitution of one nitro group in *cis*-stilbene itself; (b) the values of the molar absorptivities of the longer wave length maxima of *cis*-α-phenylchalcone (Ia) and its 3-(4-nitro) derivative Ib are much nearer to those of the corresponding *trans*-stilbenes than to those of the *cis*-stilbenes

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(5) Molar absorptivities are used as an approximate measure of integrated absorption intensities; and the wave lengths of the maxima are approximations of the true values for the chromophores being considered, which depend for accuracy upon the degree of absorption overlap by other chromophores.

(6) The alternative comparison between the *cis*-α-phenylchalcone (Ia) and the *trans*-3-(4-nitrophenyl) compound (IIb), and between the analogous *trans*-*cis* pair (IIa and Ib), involves bathochromic shifts of 41 and 25 mμ, respectively, but does not lead to any rational interpretation.

(7) (a) A. Smakula and A. Wasserman, *Z. physik. Chem.*, **155**, 353 (1931); (b) M. Calvin and R. E. Buckles, This Journal, **62**, 3324 (1940).

(8) In this discussion the treatment of the cross-conjugated chalcone system, and the stilbene system which is cross-conjugated with the chalcone system, as separate chromophores, is at best an approximation, but it is one which seems to lead to valid conclusions here.

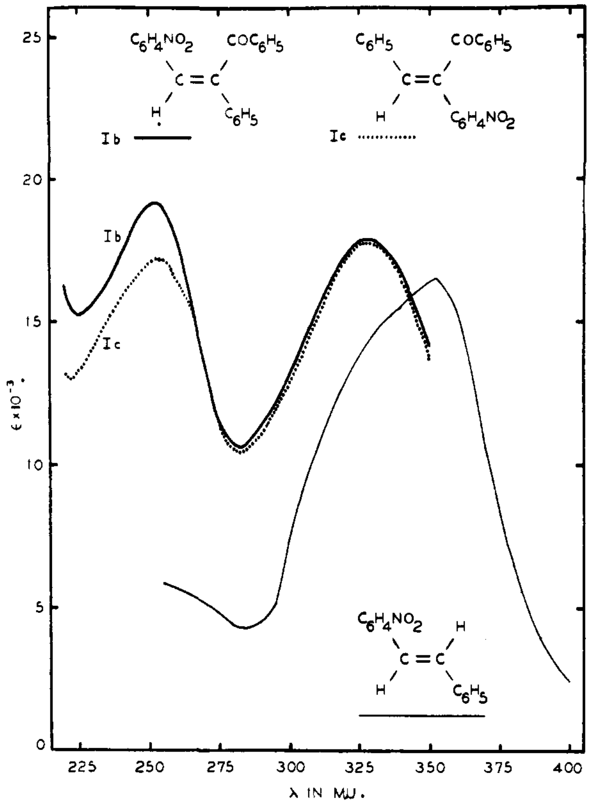

Fig. 4.—Absorption spectra of the *cis*-*p*-nitro-α-phenylchalcones (Ib and Ic).

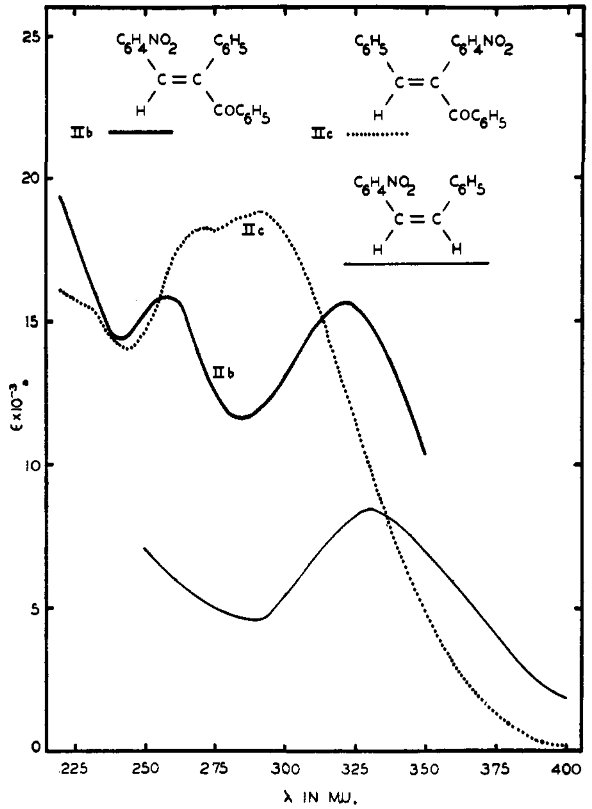

Fig. 5.—Absorption spectra of the *trans*-*p*-nitro-α-phenylchalcones (IIb and IIc).

[this point is important in the present circumstances where it is certain (as shown above) that the *trans*-stilbene system is principally involved and the chalcone contribution is small, if any[8]]; and (c) the consideration of the shorter wave length peaks brought out below under the discussion of the above observations (2) and (3).

The *trans*-chalcone (*cis*-stilbene) configurations of the stereoisomers (IIa, IIb) follow by difference from the *cis* configurations (Ia, Ib) established above, and they are supported by the following points: (a) the shift of the longer wave length maximum of 18.5 mμ in going from IIa to IIb is much smaller than that caused by *p*-substitution of a nitro group in *cis*-stilbene itself (44 mμ), and this indicates an appreciable contribution by an effective chalcone conjugation[8] [significant effectiveness of this conjugation is more logical in the *trans* compound because a greater degree of coplanarity of the chalcone part of the molecule is possible than is the case in the *cis* isomer[9]]; and (b) the following consideration of the above observations (2) and (3) concerning the molar absorptivities at longer and shorter wave length maxima.

Discussion of Observations (2) and (3).—The greater molar absorptivities at both absorption peaks of the *cis* isomers (Ia, Ib) as compared with those of the *trans* isomers (IIa, IIb) is explained in the case of the latter by the partial effectiveness of conjugation of both *cis*-stilbene and *trans*-chalcone systems, and in the former by the contrastingly predominant effectiveness of the *trans*-stilbene conjugation and ineffectiveness of the *cis*-chalcone conjugation.[8]

The longer wave length maximum of the *cis*-3-(4-nitro) compound Ib (Fig. 4) corresponds closely to the longer wave length absorption of an essentially planar *trans*-4-nitrostilbene system. The benzoyl group in such a molecule would necessarily be non-coplanar with the *trans*-4-nitrostilbene portion of the molecule, as models clearly show, and is apparently free to act as an almost completely isolated resonating unit; this should give rise to a characteristic molar absorptivity of *ca.* 14×10^3. The sum of this value (14×10^3) plus an expected contribution of 6×10^3 (at *ca.* 252 mμ) from the shorter wave length absorption of an effective *trans*-4-nitrostilbene, corresponds closely to the observed value[10] 19×10^3.

In *cis*-α-phenylchalcone (Ia), the situation seems analogous to that of the 3-(4-nitro) derivative Ib although it is not as easily recognizable from inspection of the absorption curve (Fig. 2).

The lower molar absorptivities at both the

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(9) In chalcone itself the relatively smaller degree of planarity of the *cis* as compared with the *trans* isomer is adequately shown by ultraviolet absorptions as well as by molecular models and scale drawings (see ref. 2).

(10) If the longer wave length maximum of the *cis* isomer Ib had been due to the chalcone system, the molar absorptivity at the shorter wave length maximum would have been appreciably lower because of low isolated-benzoyl character. In other words, if one should argue that for this *cis* isomer (Ia) the longer wave length maximum represents a *trans*-chalcone type resonance, the high absorptivity at the short wave length maximum cannot be explained. If, on the other hand, one argues that the longer wave length maximum represents a *cis*-chalcone resonance, then the high absorptivity at this maximum cannot be accounted for. But arguing as above, that the longer wave length maximum is due primarily to an effectively conjugated *trans*-stilbene system, the heights of both peaks can be accounted for.

longer and shorter wave length maxima of the two *trans* isomers (IIa, IIb) [as compared with those at the respective maxima of the two *cis* isomers (Ia, b)] correspond to expectations, assuming less steric interference with the *trans*-chalcone system and consequently appreciable effectiveness of this conjugation, and assuming a diminished but still significant *cis*-stilbene contribution. These interference effects are clearly evident upon examination of scale molecular models. A characteristic of *trans*-chalcone (III, Fig. 1) is the very low molar absorptivity in the benzoyl group range 240–250 mμ, and this would account for the somewhat lowered absorptivity at the shorter wave length peak. The very considerable steric interference with planarity of both of the principal chromophores would account for the relatively low molar absorptivity at the longer wave length maximum. And the molar absorptivities at the longer wave length maxima of the *trans* isomers (IIa, IIb), although considerably lower than the comparable maxima of the *cis* isomers (Ia, Ib), are still considerably higher than those for the parent *cis*-stilbene and *cis*-*p*-nitrostilbene (Fig. 3, 5), respectively, which also is consistent with a significant contribution by the *trans*-chalcone system.[8]

The α-(4-Nitrophenyl)-chalcone Isomers (Ic, IIc).—The study of these compounds, where the nitro group cannot be involved in chalcone-type resonance proved to be consistent with, and to lend additional support to, the foregoing conclusions. The curve of the long wave length peak of the *cis* isomer (Ic) was found to be almost superimposable on that of the *cis* 3-(4-nitro) analog Ib (Fig. 4). This proved unequivocally that the longer wave length maxima of both nitro compounds (Ic and Ib), and by close analogy the longer wave length maximum of the parent compound (Ia) also, are due entirely to the effective conjugation of the 4-nitrostilbene system and do not involve significant contributions by the chalcone system. If the resonance of the *cis*-chalcone system were appreciable in these isomers, analogy indicates that there would have been a considerably higher molar absorptivity at the longer wave length maximum in the 3-(4-nitro)-α-phenylchalcone (Ib) than in the 2-(4-nitro) isomer Ic, because *cis*-4-nitrochalcone itself has its molar absorptivity at 16.2 $\times$ 10^3 as compared with 8.8 $\times$ 10^3 for the parent *cis*-chalcone (see Fig. 1).

The comparison of the spectra of the *trans* compounds (IIc, IIb) (Fig. 5) is not as significant as that of the spectra of the *cis* compounds (Ic, Ib), but the actual differences in the electronic natures of the two *trans* compounds are not so great as the curves would at first glance seem to indicate. It must be noted that expectation of a small bathochromic shift of the long wave length peak such as is produced by the nitro group in conjugation with the chalcone system of IIb, does not apply in the case of IIc; thus if the relative contributions of the *cis*-stilbene and *trans*-chalcone systems were the same in IIb and IIc there presumably would have been a hypsochromic shift. Any apparent hypsochromic shift would appear to be exaggerated when this maximum gets near the shorter wave length maximum, and the actual shift could be determined only by graphical resolution of the observed single bifurcated peak into its component bands. In spite of the difficulty in analyzing the spectra it would appear nonetheless, that there is more chalcone contribution involved in the spectrum of IIc than in the spectrum of IIb.

Relative Chemical Reactivities of the *cis* and *trans* Isomers.—If the conclusions drawn from spectroscopic studies are correct the *trans* isomers II should show nucleophilic reactivity to a relatively high degree, whereas the *cis* isomers I should show stilbene character and markedly lowered or no chalcone reactivity. There are some obvious addition reactions by which such differences in reactivities might be observed and determined. Ordinary chalcones undergo nucleophilic 1,4-additions easily (such as the Michael reaction, and additions of hydrogen halides, amines, the Grignard reagent and the like), whereas stilbenes do not undergo these types of additions easily if at all. The determination of the relative facility of some of these reactions with the *cis*- and *trans*-α-phenylchalcones should serve as a good test of our conclusions. Several such reactions in this field have already been reported by Stobbe, and these reactions, together with an additional one which we have found, are entirely in accord with theory.

Stobbe carried out reactions on both isomers of α-phenylchalcone[11] but he made no effort to relate his data to the configurations or to the effectiveness of the conjugated systems involved. He claimed to have found three isomers in the 3-(4-nitro) series, and of these he assumed two to have the same configuration.[3a] (We have now shown these two to be *cis* and *trans* isomers (Ib, IIb), and have demonstrated to our satisfaction that the so-called "third isomer" was in error.[3b]) Stobbe's object was to produce isomeric products from two isomeric starting materials, but in each reaction which he studied he obtained only one and the same product from either isomer.

He found that one of the isomeric α-phenylchalcones (which we now designate as *trans* IIa) reacted more rapidly than did the other (which we designate as *cis* Ia) in all reactions tried except bromination where he gave no relative rate data; and he concluded that the one isomer (*cis*, Ia) which reacted the more slowly underwent isomerization first (to *trans* IIa), and that this rearrangement was followed by the addition reaction. Isolation of the opposite isomer from the partially reacted mixture in the reactions with bromine and with hydrogen chloride demonstrated that in these two cases isomerization actually does occur in the presence of these reagents; and in agreement with this we have found that when bromine was added in small amounts, the *trans* isomer IIa reacted much faster at first than did the *cis* isomer Ia but that as the reaction proceeded addition continued at the same rate in both experiments.

It should be noted that the difference in the facility of addition of the electrophilic reagent, halogen, to chalcones and derivatives, as compared with the addition of this reagent to the stilbenes,

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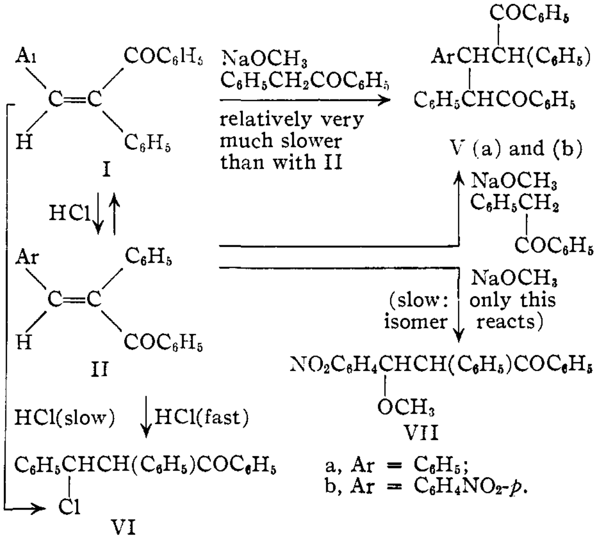
[11] H. Stobbe and K. Niedenzu, *Ber.*, **34**, 3897 (1901).

is not nearly as great as the very significant difference in the facility of addition of nucleophilic reagents to the two types of compounds. However, a more exact and detailed comparison of bromination rates, although of incidental interest, did not seem pertinent to the present problem and has not been attempted.

In the base-catalyzed nucleophilic addition of desoxybenzoin to the α-phenylchalcones Stobbe[3a,11] found the difference in the rates of reaction to be very great. The lower-melting α-phenylchalcone (now known to be *cis* Ia) was recovered unchanged when subjected to conditions under which the other isomer (*trans*, IIa) reacted to give the addition compound Va in 30% yield. Only under much more drastic and prolonged conditions could he make the *cis* compound react and then only with very poor yield of the addition product. In the case of the 3-(4-nitro) compound one isomer (to which we now assign the *cis* configuration Ib) gave only 12% yield of the addition compound Vb in two days, whereas the other (the *trans* isomer IIb) gave an 88% yield within several hours. An experiment done by us showed that the *cis* isomer Ib did not undergo any isomerization whatsoever in 24 hours in the presence of sodium methoxide, but the *trans* isomer IIb, which was recovered largely unchanged and gave no isomerization, did give a small but significant yield of the methanol addition compound VIIb, the result of nucleophilic attack by methoxide ion. Thus the conclusions about the configurations of the α-phenylchalcones arrived at on the basis of ultraviolet absorptions are consistent with the relative reactivities of the two types of compounds. The *cis* compounds with their *trans*-stilbene structures and ineffectively conjugated *cis*-chalcone systems are resistant toward attack by nucleophilic agents; and the *trans* compounds in which the *trans*-chalcone system present is less sterically impeded and more effectively conjugated, are normally reactive in this sense.



The relative facility of addition of hydrogen chloride to *cis*- and *trans*-α-phenylchalcones also is consistent with and supports the configurational assignments based on the spectroscopic studies. This reagent normally does not form stable addition compounds with stilbenes[12] but does add to ordinary chalcone systems. The α-phenylchalcone which has been shown to have the *cis* configuration Ia reacts appreciably slower with hydrogen chloride than does the other isomer (*trans*, IIa),[11] and gives the addition compound VI.

The very marked rate differences in the additions to the *cis*- and *trans*-α-phenylchalcones considered together with the fact that hydrogen chloride is known to isomerize the *cis* to the *trans* isomer, and in the absence of evidence indicating that either the desoxybenzoin or the methoxide ion causes isomerization, lends considerable support to the argument that isomerization from *cis* to *trans* is necessary for a reasonable rate of addition and that addition occurs readily only to the *trans* isomer.

It should be noted that simple steric inhibition of reaction at the β-carbon of the chalcone systems might be greater in one configuration than the other and might conceivably be the responsible and governing factor. Interpretation on this basis would lead to the same conclusions as above, because if the effect were appreciable, the hindrance should be greater in that chalcone configuration having the lowest degree of planarity. However, Kohler has demonstrated the lack of effective hindrance toward 1,4-addition of the Grignard reagent to chalcones even when the 3-aryl group is mesityl, unless the β-position is fully substituted[13]; and conversely, therefore, one would not expect hindrance at the β-carbon of the α-phenylchalcone systems under consideration here, to be a decisive factor affecting the additions.

The favored reactivity of the *trans* isomer of α-phenylchalcone toward phenylhydrazine, at the carbonyl group, reported by Stobbe, serves as a quite different type of differentiation between the *cis* and *trans* isomers, which is also consistent with theory. This effect is understood when one considers how the carbonyl group of the *cis* isomer must be compressed between the two phenyls of the effectively planar stilbene system, with the carbonyl carbon effectively boxed in and completely shielded from nucleophilic attack by the reagent (this is clearly visualized upon inspection of molecular models). On the contrary, in the more reactive *trans* compound the carbonyl carbon is relatively open to attack.

The base-catalyzed reaction of hydrogen peroxide goes well with conjugated systems such as in *trans*-chalcone and dibenzoylethylene,[14] and is not commonly reported for ordinary olefins. *cis*-Chalcone with its relatively lowered α,β-unsaturated carbonyl effectiveness and more "aliphatic" ethylene double bond character, should be less reactive toward this reagent. Experiment shows this to be true.[15] Although both isomers react

[12] P. B. Levine and L. A. Mikeska, *J. Biol. Chem.*, **65**, 507 (1925).

[13] E. P. Kohler and L. W. Blanchard, THIS JOURNAL, **57**, 367 (1935).

[14] (a) E. P. Kohler, N. K. Richtmyer and W. F. Hester, *ibid.*, **53**, 213 (1931); (b) R. E. Lutz and F. N. Wilder, *ibid.*, **56**, 1987 (1934); (c) E. Weitz and A. Scheffer, *Ber.*, **54**, 2327 (1921); (d) W. A. Waters, "Organic Chemistry," H. Gilman (editor), J. Wiley and Sons, Inc., New York, N. Y., Vol. IV, 1953, p. 1172.

[15] These experiments were performed in this Laboratory by Mr. James O. Weiss and were based on a preliminary observation by Dr. R. H. Jordan.

readily, the *cis* isomer reacts at a significantly lower rate and gives the same oxide (stereoisomers are possible); however, it has not been determined whether or not rearrangement of the labile *cis* to the stable *trans* form occurs during the reaction with the *cis* compound.

Further studies on *cis–trans* differences in these types of compounds are in progress.

Acknowledgement.—The experiments in this laboratory on the action of hydrogen peroxide on *cis*- and *trans*-chalcones were performed by Mr. James O. Weiss and were based on a preliminary observation by Dr. Robert H. Jordan concerning relative rates of reaction.

Experimental[16]

Ultraviolet absorption spectra were made using a Beckman DU quartz spectrophotometer on two samples of each compound, weighed out separately and run on separate days to minimize errors and to obtain checks, at concentrations of 0.00005 *m* in 95% ethanol. Isoöctane or another hydrocarbon solvent was not used because of the insolubility of the two isomeric 3-(4-nitro)-α-phenylchalcones. A photoequilibrium for each stereoisomeric pair, under illumination by a General Electric R. S. Sunlamp, was shown, starting from each isomer of each pair, but data will be published later along with similar data on other *cis–trans* pairs of chalcones which are now being studied. When the dilute solutions of each of the *cis* and *trans*-α-phenylchalcones (Ia, IIa) which had been brought to photoequilibrium were exposed for considerably longer periods of time (over a half-hour), a large increase in absorption in the 250–260 mμ region was noted in each case, bringing the molar absorptivities to approximately 30 $\times 10^3$, but nothing has been done relative to isolation of the products responsible for these absorptions. The same phenomenon was observed also in the case of the 2-(4-nitrophenyl)-chalcone isomers (Ic, IIc); however, over one hour of exposure to the sunlamp was necessary.

Ultraviolet absorptions determined by us for comparisons and as checks on the literature values are as follows: *cis*-chalcone, λ_{max} 250 and 292.5 mμ, ϵ 13.7 and 8.8 $\times 10^3$; *trans*-chalcone, λ_{max} 227.5 and 307.5, ϵ 9.8 and 24.3 $\times 10^3$ (made by Dr. C. L. Browne in this Laboratory; *cf.* ref. 2a).

cis-**4-Nitrochalcone (IV)**.—Dilute (0.004 *M*) solutions of the *trans* compound[17] in benzene were exposed to sunlight or sunlamp for several hours and for varying additional periods of time. The solutions turned much yellower because of the formation not only of the *cis* isomer but also deeply yellow by-products which appear in varying degrees in sunlight inversions of all the chalcones we have thus far studied. Recrystallizations of the products from these experiments showed no large differences in results. The *cis* isomer crystallized as light yellow needles which always grew on crystals of the *trans* isomer, thus rendering separation quite difficult. For crystallizations benzene–isoöctane and benzene–petroleum ether solvent pairs were unsatisfactory. Some success was achieved by very slow evaporation of solutions in ethanol in which the *cis* isomer is more soluble. The small amounts of pure product obtained were sufficient for our immediate purpose and practical preparative directions have not yet been worked out; m.p. 98–98.5°, λ_{max} 262.5 and 297.5–300 mμ, ϵ 12.4 and 16.1 $\times 10^3$.

Anal. Calcd. for $C_{15}H_{11}NO_3$: C, 71.14; H, 4.38. Found: C, 70.90; H, 4.47.

trans-**4-Nitrochalcone** (IV)[4]: m.p. 164–164.5° (lit. 162.5°),[17] λ_{max} 315–317.5 mμ (A, 317[4]), ϵ 28.2 $\times 10^3$.

Preparation of Chlorobenzyldesoxybenzoin (VI).—Two attempts following the Stobbe procedure,[11] using freshly distilled benzaldehyde, gave no chlorine-containing product. Compound VI was obtained by passing hydrogen chloride for 3.75 hours into a solution of 10 g. of desoxybenzoin in 50 g. of practical grade benzaldehyde (a molar ratio of 1:10 instead of the 1:2 of Stobbe[11]); m.p. 175–176° (Stobbe[11] 170–172°).

Preparation of *trans*-**α-phenylchalcone (IIa)** was effected by adding the calculated amount of aqueous sodium hydroxide slowly over 20 min. to a refluxing acetone solution of VI; m.p. 103–103.5° (Stobbe[11] 101–102°), λ_{max} 255 and 300–302.5 mμ, ϵ 15.1 and 13.7 $\times 10^3$. The *cis*-**isomer**[11] **(Ia)**: m.p. 88–89°, λ_{max} 260 and 280 mμ, ϵ 24.6 and 22.9 $\times 10^3$.

Whenever mixtures of a pair of α-phenylchalcone isomers were encountered from condensation reactions or interconversions of the isomers, the following *separation technique* was employed. The dry solid or oil was taken up in a slight excess of benzene at room temperature and the solution was filtered through a sintered glass funnel if any dust or undissolved matter was present; this was to prevent premature crystallization. (Clean glassware was essential.) Isoöctane was added to the approach of the saturation point with respect to the isomers, always with care to avoid starting crystallization prematurely. (Stobbe[3a] had used petroleum ether but we found isoöctane to be much more satisfactory.) The solutions were allowed to stand at room temperature for a few minutes and more isoöctane was added if necessary, and they were allowed to evaporate over a period of 1–3 days, depending on the difficulty of individual crystal growth. When a second type of crystal started to form the solution was decanted carefully into another container. Often both types of crystals came down together (each in its own distinctively individual form), depending on relative solubilities and on the ratio of the amounts of each present, and in such cases separation was accomplished manually (this method frequently was used).

Preparation of *cis*- **and** *trans*-**3-(4-nitro)-α-phenylchalcone**[3a] **Ib**: m.p. 168.5–169.5° (Stobbe[3a] 164–165°), λ_{max} 251–252.5 and 327.5 mμ, ϵ 19.2 and 17.9 $\times 10^3$. **IIb**: m.p. 153–153.5° (Stobbe[3a] 148–149°), λ_{max} 256.5–257.5 and 321 mμ, ϵ 15.9 and 15.7 $\times 10^3$.

cis **and** *trans*-**2-(4-Nitro)-α-phenylchalcones (Ic, IIc**[18]**)**.—Hydrogen chloride was passed into a solution of 15 g. of 4-nitrobenzyl phenyl ketone in 50 g. of benzaldehyde for 3.5 hours. The mixture was taken up in benzene and washed several times with water. After evaporation the residue was dissolved in a small amount of benzene at room temperature, and fractional crystallization was effected by addition of isoöctane and allowing the solution to evaporate slowly. A small first crop (about 5%), the *trans isomer* (IIc) (small light yellow short prisms), upon crystallization first from ethanol and then from benzene–isoöctane, melted at 188–189.5°; λ_{max} 272.5 and 290–292.5 mμ, ϵ 18.3 and 18.7 $\times 10^3$.

Anal. Calcd. for $C_{21}H_{15}NO_3$: C, 76.58; H, 4.59. Found: C, 76.78; H, 4.48.

A small second crop (about 5%), the *cis isomer* (Ic), was deeper yellow in color and was very different and distinctive in crystal form (long needles); it was recrystallized from benzene–isoöctane; m.p. 135.5–136°, λ_{max} 252.5 and 327.5 mμ, ϵ 17.2 and 17.7 $\times 10^3$. The compound held solvent of crystallization persistently and the carbon analyses of samples dried at room temperature or at 56° under *vacuo* were consistently 1.4 to 1.5% above theory.

Anal. (sample dried at 100° for several hours at 0.1 mm. pressure): Calcd. for $C_{21}H_{15}NO_3$: C, 76.58; H, 4.59. Found: C, 76.91; H, 4.67.

The bulk of the residual material in the above preparation was a mixture which was not investigated further once usable samples of the isomers had been obtained.

Sunlight interconversions in either direction were done by exposure of 10^{-2} *M* benzene solutions to the sunlight or sunlamp for 6–8 hours. The mixtures obtained in both cases were shown by actual separations by fractional crystallizations to contain about the same 1:3 ratio of *cis* to *trans* isomers. Samples thus isolated were identified by mixture melting points with reference samples obtained in the original condensation. Practically no deterioration of the two isomers was noted during these manipulations.

It was noted that photoequilibria at 10^{-5} *M* concentrations, determined spectrophotometrically, were in approximate (qualitative) agreement with these photoequilibria at more concentrated solutions (10^{-2} molar).

1,2-Diphenyl-3-(4-nitrophenyl)-3-methoxypropanone-1 (VII).—A solution of 0.2 g. of the *trans*-chalcone IIb and 0.02 g. of sodium methoxide in 200 ml. of methanol was al-

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[16] Microanalyses were by Mrs. C. Z. Jeffries, Miss Patricia L. Paynter and Clark Microanalytical Laboratories.

[17] H. Wieland, *Ber.*, **37**, 1149 (1904).

[18] This compound was made recently by the action of *p*-nitrobenzenediazonium chloride on chalcone; P. L'Ecuyre and C. A. Olivier, *Can. J. Research*, **28B**, 648 (1950).

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.

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[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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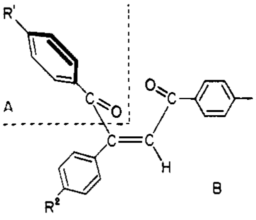
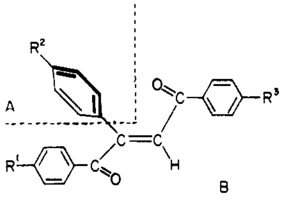
The selectivity of the shift in ultraviolet absorption maxima caused by *p*-monosubstituents, methyl and phenyl, in *cis* and *trans*-dibenzoylstyrenes constitutes supporting evidence for the postulated conformations with respect to effective relative planarities of the principal parts of the conjugated 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.

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.



I *cis*



II *trans*

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

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

(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.* also (d) W. B. Black and R. E. Lutz, *ibid.*, **75**, 5990 (1953).