The Photochemistry of Dibenzoylethylenes. Mechanistic and Exploratory Organic Photochemistry. XXII[1]

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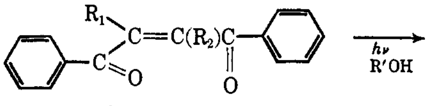
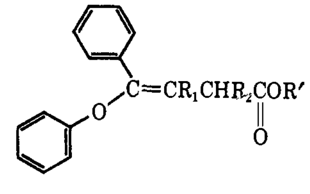
Abstract: The new photochemical rearrangement of dibenzoylethylenes is now reported in full detail. Dibenzoylethylene, dibenzoylstyrene, and dibenzoylstilbene afforded, on irradiation in alcoholic solvent, the esters of 4-phenyl-4-phenoxy-3-butenoic acid, 2,4-diphenyl-4-phenoxy-3-butenoic acid, and 2,3,4-triphenyl-4-phenoxy-3-butenoic acid, respectively. The reaction involves a 1,5 phenyl migration from carbon to oxygen. In the case of dibenzoylethylene the reaction was shown to proceed at least 90% by way of the singlet and up to 10% *via* the triplet by means of sensitization experiments. For the dibenzoylstilbene rearrangement, the singlet was again shown to play the dominant role. A detailed mechanism is advanced which accounts for the selectivity observed for the dibenzoylstyrene rearrangement and is supported by the finding that it is the *cis*-reactant isomers which rearrange.

In our preliminary communication[3] we reported a previously unobserved rearrangement of dibenzoylethylenes. Dibenzoylethylene (**1**) itself was found to afford ethyl 4-phenyl-4-phenoxy-3-butenoate (**2**) when irradiated in 95% ethanol. Dibenzoylstyrene (**3**) gave ethyl 2,4-diphenyl-4-phenoxy-3-butenoate (**4**) and 2,4-diphenyl-4-phenoxy-3-butenoic acid (**5**). Independently, Griffin[4] reported the rearrangement of dibenzoylethylene (**1**). Subsequent to our communication[3] we have extended the reaction to the rearrangement of dibenzoylstilbene.[5]



1, $R_1, R_2 = H$
3, $R_1 = H$; $R_2 = Ph$
6, $R_1, R_2 = Ph$



2, $R_1, R_2 = H$; $R' = Et$ (ref 3,4)
4, $R_1 = H$; $R_2 = Ph$; $R' = Et$ (ref 3)
5, $R_1 = H$; $R_2 = Ph$; $R' = H$ (ref 3)
7, $R_1, R_2 = Ph$; $R' = Me$

The present publication describes our preliminary findings in detail and delineates the reaction mechanism.

The Rearrangement and Evidence for Product Structures. It was observed that irradiation of the *cis* isomers of dibenzoylethylene (**1**), dibenzoylstyrene (**3**), and dibenzoylstilbene (**6**) afforded products (**2**, **4**, and **7**, respectively) analyzing for starting material plus one molecule of the methanol, ethanol, or *t*-butyl alcohol solvent. Evidence for the above structures was derived from elemental analysis, spectral information, and degradation.

In addition to the elemental analysis, the infrared and nmr spectra were consistent with the assigned structures. Each infrared had an ester carbonyl in the 5.75–5.80-μ region. The nmr spectrum of **2** possessed a typical AX_2 pattern, having a vinyl triplet at τ 4.00 and a methylene doublet at τ 7.78 (J = 7 cps). The aromatic protons absorbed at τ 2.4–3.4. The ethoxy group displayed the normal quartet at τ 5.90 and triplet at τ 8.80 (J = 7 cps). The relative intensities for the preceding were 1:2:10:2:3 as expected.

Consistent with the assigned structure of **4**, the nmr spectrum displayed an AB quartet with doublets at τ 3.74 and 5.29 (J = 11 cps). The aryl absorption from τ 2.4 to 3.4 and the ethoxy pattern of a quartet at τ 5.99 and a triplet at τ 8.99 were also observed. The relative intensities were 1:1:15:2:3.

Finally, the nmr spectrum of **7** was simply a multiplet at τ 2.7–3.3 corresponding to the aromatic absorption, a methine singlet at τ 4.78, and a methoxy singlet at τ 6.60 (relative intensity 20:1:3).

Corroborative evidence for structures **2**, **4**, and **7** was obtained from degradation by acid hydrolysis as outlined in Chart I. From each degradation, phenol was isolated in addition to a known, substituted benzoylpropionic acid. These were shown to be 3-benzoylpropionic acid,[6] 2-phenyl-3-benzoylpropionic acid,[7] and 2,3-diphenyl-3-benzoylpropionic acid,[8] by comparison with authentic samples.[9]

The Reaction Mechanism. Structural Aspects. The general pathway proposed in our preliminary communication[3] is shown in Chart II. This assumes an n–π^* excited state and accounts for the observed products. It is in accord with the general idea of n–π^* excited states possessing a partially occupied, thereby electron-deficient, p_y orbital capable not only

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[1] For paper XXI see H. E. Zimmerman and J. S. Swenton, *J. Am. Chem. Soc.*, **89**, 906 (1967).

[2] (a) Research Associate, University of Wisconsin, 1961–1962; (b) National Institutes of Health Predoctoral Fellow, 1964–1966; (c) National Institutes of Health Predoctoral Fellow, 1961–1964.

[3] H. E. Zimmerman, H. G. C. Dürr, R. G. Lewis, and S. Bram, *J. Am. Chem. Soc.*, **84**, 4149 (1962).

[4] G. W. Griffin and E. J. O'Connell, *ibid.*, **84**, 4148 (1962).

[5] H. V. Halben, H. Schmidt, and M. Hochweber, *Helv. Chim. Acta*, **30**, 1135 (1947), reported a photochemical rearrangement of tetrabenzoylethylene which affords a different type product.

[6] S. Gabriel and J. Coleman, *Ber.*, **32**, 398 (1899).

[7] Y. Akhnookh, W. I. Awad, and F. G. Baddar, *J. Chem. Soc.*, 1013 (1959).

[8] H. M. Crawford, *J. Am. Chem. Soc.*, **60**, 3078 (1938).

[9] Subsequent to completion of our nonmechanistic efforts on the dibenzoylstilbene rearrangement, the reaction has been reported by A. Padwa, D. Crumrine, and A. Shubber, *ibid.*, **88**, 3064 (1966).

of hydrogen abstraction[10–12] but also of attacking π systems.[13]

Chart I

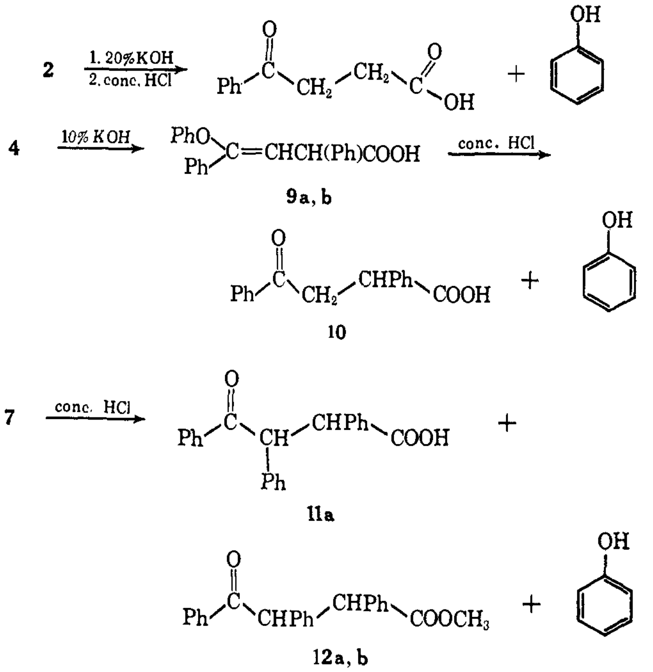
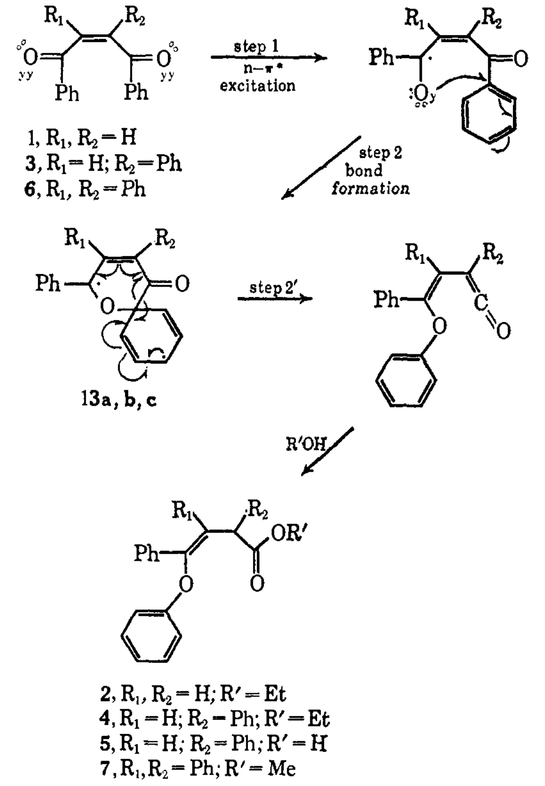


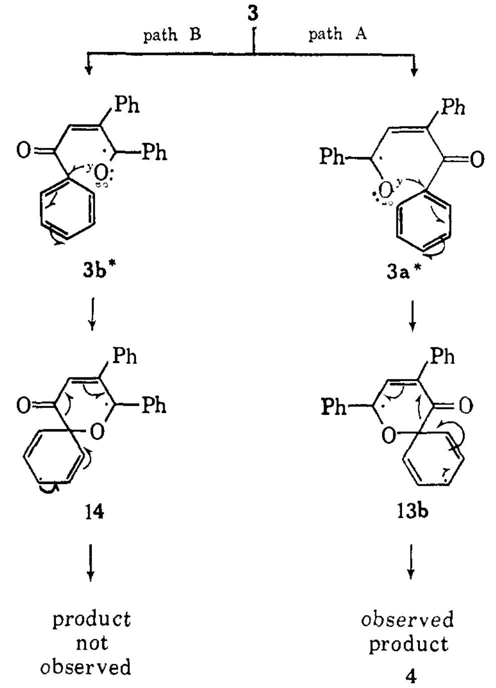
Chart II



Evidence for the gross mechanism was found in the stereochemical requirements of the reaction. The mechanism outlined demands the *cis*-reactant stereoisomer for attack of the excited benzoyl oxygen on the other benzoyl phenyl group. In agreement with this it was found that with low conversions[14] irradiation of solutions of *trans*-dibenzoylethylene gave no detectable rearrangement; these conditions did give product from *cis* reactant. Only after an appreciable quantity of the *cis* reactant had formed was the product noted.

Another interesting aspect of the reaction was the selectivity found in the dibenzoylstyrene rearrangement. *A priori* two pathways are possible, since either of the benzoyl phenyl groups might migrate (note Chart III). Different rationales, not totally independent, can explain this result. First, two n–π* excited states are possible, **3a*** and **3b***. However, **3a*** is better able to delocalize the odd electron in the π system owing to direct conjugation of the styryl phenyl group (note the greater number of resonance contributors to **3a*** than to **3b***). Further along in the reaction this difference in electronics is again apparent in the half-migrated intermediates **13b** and **14**. The species deriving from **3a*** has greater electron delocalization and is of lower energy. We note that it is this pathway which leads to the observed product.[15]

Chart III



A further comment is relevant, namely that *cis–trans* isomerization occurs in each of these systems and at a rate somewhat faster than the rearrangement.[14,17] It has been

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(10) H. E. Zimmerman, 17th National Organic Chemistry Symposium, Bloomington, Ind., June 1961, Abstracts, p 31.

(11) H. E. Zimmerman, *Advan. Photochem.*, **1**, 183 (1963).

(12) M. Kasha, *Radiation Res. Suppl.*, **2**, 243 (1960); W. D. McElroy and B. Glass, Ed., "Light and Life," Johns Hopkins University Press, Baltimore, Md., 1961, p 31.

(13) H. E. Zimmerman, *Science*, **153**, 837 (1966), paper XIX of the series.

(14) The amount of *cis*-dibenzoylethylene formed from isomerization averaged 13% in the runs beginning with the *trans* isomer. The amount of rearrangement product expected from this absorbing light is just below the threshhold of detection.

(15) (a) What controls the direction of the excited-state transformations in general is uncertain. Rate of conversion from excited to ground state has been considered by Hammond[16] as possibly controlling in some cases. Another factor considered[13] in many cases is the tendency of an excited species to avoid energy maxima and to minimize its energy prior to conversion to ground-state product. The latter factor seems to rationalize the present selectivity. (b) A second driving force which might be superimposed on the electronic one discussed has been suggested by G. S. Hammond (private communication). Thus in path B there is greater van der Waals repulsion due to phenyl–phenyl proximity.

(16) G. S. Hammond, Photochemistry Symposium, I.U.P.A.C., discussion, Strasbourgh, France, July 1964, quoted in ref 13.

reported that this isomerization takes place in the triplet manifold.[18]

The Reaction Multiplicity. Sensitization. Having elucidated the gross rearrangement mechanism, we turned our attention to the electronic details. Let us first consider which electronic states are available. As was noted by us earlier,[3] and also by Griffin,[4] the lowest energy singlet is clearly n–π^* for *cis*-dibenzoylethylene. The absorption spectrum in hydrocarbon solvents showed the n–π^* band at 350–400 mμ (72 kcal/mole estimated for 0–0). A decided blue shift in more polar hydroxylic solvents was observed. This and the relatively low extinction coefficient (*ca.* 150) clearly are consistent with the n–π^* singlet transition assignment. Filters were used in all irradiations which effectively removed all light below 310 mμ and that above 360 mμ. Since the π–π^* transition is at 257 mμ (110 kcal/mole), the n–π^* singlet is the lowest energy state of this multiplicity. It is the first populated in the reaction sequence.

With regard to the triplet, the n–π^* configuration should be no higher than 68 kcal/mole above ground state, since most n–π^* singlet–triplet splittings will be in the range of 1400–2500 cm^{-1} with a few cases approaching 3000 cm^{-1}.[19,20] The π–π^* singlet–triplet splitting is much larger but varies considerably with structure. This aspect will be considered later.

Phosphorescence emission at 77°K from the three dibenzoylethylenes could not be detected, which is in accord with Griffin's report.[4] Thus, we are able to conclude that the n–π^* configuration is lowest in energy in the singlet manifold, while in the triplet manifold the configuration remains questionable (*vide infra*).[21]

This information allowed us to consider sensitizers and quenchers needed to determine multiplicity. Acetophenone has proven to be a useful sensitizer in these laboratories.[1,22] Its volatility allows easy removal after reaction as needed for quantitative studies. Its 73-kcal/mole triplet energy seemed certain to assure triplet transfer to the dibenzoylethylenes (*vide supra* for 68-kcal/mole energy upper limit) with triplet transfer on every collision.[23]

The choice of a solvent was considered next. Secondary alcohols seemed likely to offer special difficulties since hydrogen abstraction is known to be facile from the carbinol carbon.[25] The rate of this abstraction can easily be competitive with diffusion-controlled triplet energy transfer.

Thus, the bimolecular rate of hydrogen abstraction from 2-propanol by benzophenone triplet has been reported by Cohen[27] as 6 $\times$ 10^5 l. mole^{-1} sec^{-1}, corresponding to a pseudo-unimolecular rate of 8 $\times$ 10^6 sec^{-1}. Acetophenone is comparable.

The rate of diffusion-controlled, triplet energy transfer to acceptors such as the dibenzoylethylenes will be about 10^9 l. mole^{-1} sec^{-1},[27] and at practical concentrations of reactant (*i.e.*, about 0.001 *M* but certainly not over 0.01 *M*[28]) the pseudo-unimolecular rate constant for energy transfer is between 10^6 sec^{-1} (for 0.001 *M*) and 10^7 sec^{-1} (for 0.01 *M*).

We note that hydrogen abstraction at best is competitive and at worst is dominant. Furthermore, one might worry about the species $Ph_2\dot{C}\text{–}OH$, $Ph(CH_3)\dot{C}\text{–}OH$, and $(CH_3)_2\dot{C}\text{–}OH$ being good hydrogen donors capable of transferring hydrogen to the dibenzoylethylenes.[29]

Therefore, *t*-butyl alcohol–benzene was used as a solvent[30] for sensitization experiments carried out on both dibenzoylethylene and dibenzoylstilbene. In the case of dibenzoylethylene, the concentrations were adjusted such that acetophenone captured better than 97% of the incident light (note Experimental Section). Direct and sensitized irradiations were run under otherwise identical conditions (*i.e.*, time, solvent, filter, light source). It was observed (see Table I) that 0.10 as much *t*-butyl 4-phenyl-4-phenoxy-3-butenoate was formed in the sensitized irradiations as in the direct runs.

Table I. Comparison of the Sensitized and Unsensitized Irradiation of Dibenzoylethylene

Run	*cis*-Dibenzoylethylene, mmoles	Additive	Product yield, mmole	Rel. yield
1^b	4.15	None	0.401	1.00
2^b	1.50	Acetophenone^a	0.051	0.133^d
3^c	4.08	None	0.440	1.00
4^c	1.33	Acetophenone^a	0.057	0.129^d

^{a} Acetophenone (0.285 *M*) absorbed 97% of the light in these runs. ^{b} 4-hr run. ^{c} 7-hr run. ^{d} This is 0.10 when corrected for light absorbed by dibenzoylethylene.

One might concern himself about the possibility of there being a higher concentration of the reactive *cis* isomer present in the direct irradiations compared with the sensitized runs. If this were the case, then the low conversion in the sensitized runs could just be due to low concentrations of the reactive *cis* reactant. In fact, if anything, the converse is the case. Inspection

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[17] R. E. Lutz and W. J. Welstead, Jr., *J. Org. Chem.*, **27**, 2763 (1962). Lutz has studied the photochemical *cis–trans* isomerization of dibenzoylstilbene in which he noted some "deterioration of material." Possibly, this could have been our observed rearrangement.

[18] G. Cauzzo, U. Mazzucato, and A. Foffani, *Bull. Soc. Chim. Belges*, 71, 838 (1962).

[19] G. Zimmerman, Ph.D. Thesis, University of Wisconsin, 1965.

[20] J. Sidman, *J. Chem. Phys.*, **27**, 429 (1957).

[21] This latter contrasts with our earlier statement in the preliminary communication.[3]

[22] H. E. Zimmerman, R. G. Lewis, J. J. McCullough, A. Padwa, S. Staley, and M. Semmelhack, *J. Am. Chem. Soc.*, **88**, 1965 (1966).

[23] Where the transfer is exothermic by 3 kcal/mole or more, this will be diffusion controlled.[24]

[24] (a) H. L. J. Bäckstrom and K. Sandros, *Acta Chem. Scand.*, **12**, 823 (1958); (b) F. Wilkinson, *J. Phys. Chem.*, **66**, 2569 (1962).

[25] Acetophenone has been known to photoreduce to the acetophenone pinacol in 1-butanol, cyclohexanol, phenylmethylcarbinol, ethanol, and 2-propanol [C. Weizman, E. Bergmann, and Y. Hirshberg, *J. Am. Chem. Soc.*, **60**, 1530 (1938)]. Benzophenone also forms benzophenone pinacol in secondary alcohols.[26]

[26] (a) W. Moore, G. S. Hammond, and R. P. Foss, *ibid.*, **83**, 2789 (1961); (b) J. N. Pitts, R. L. Letsinger, R. P. Taylor, J. M. Patterson, G. Recktenwald, and R. B. Martin, *ibid.*, **81**, 1068 (1959).

[27] The bimolecular rate of hydrogen abstraction from 2-propanol has been determined by S. G. Cohen, D. A. Laufer, and V. Sherman, [*ibid.*, **86**, 3060 (1964)] to be 6 $\times$ 10^5 l. mole^{-1} sec^{-1} and the molarity of 2-propanol as a solvent is 13 *M*.

[28] The concentration of reactant is limited both by solubility and by the necessity that it not compete effectively for light with the sensitizer. Thus at 0.01 *M*, one would need 85 g/l. benzophenone or 195 g/l. of acetophenone to capture 97% of the light. Clearly, this is impractical.

[29] For example, the ability of the hydroxyisopropyl radical to transfer hydrogen is seen in the quantum yield of two reported by Pitts[26b] where in dilute solution the hydrogen is transferred to a second benzophenone molecule.

[30] *t*-Butyl alcohol has been shown to be an inefficient donor in hydrogen abstraction [D. S. Kendall and P. A. Leermakers, *J. Am. Chem Soc.*, **88**, 2766 (1966)].

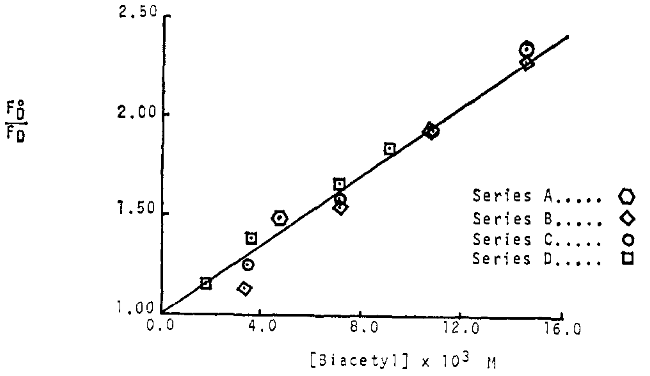

Figure 1. Stern–Volmer plot of the quenching of *cis*-dibenzoylstilbene fluorescence (*cf.* Table II).

of the nmr spectra from the direct and sensitized runs revealed that the intense peak due to the *trans*-vinyl absorption (478 cps downfield from TMS) was present to a slightly smaller extent in the sensitized than the direct run.

Thus, the triplet, when generated independently, rearranges only 10% as efficiently as directly excited dibenzoylethylene. These experiments show by exclusion that the singlet plays the dominant role in the rearrangements.[31]

Sensitization experiments were carried out on *cis*-dibenzoylstilbene in the same manner although, in this particular case, the per cent incident light captured by acetophenone was not as high (estimated at 80%) owing to an unfavorable ratio of extinction coefficients. The ratio of *t*-butyl 4-phenoxy-2,3,4-triphenyl-3-butenoate produced with and without sensitization was 0.45. This is higher than the ratio of the true sensitized to direct efficiency due to some light absorption by reactant in the sensitized run.

As before it turns out that under the conditions of the comparison runs there was more of the reactive *cis* isomer in the sensitized than in the direct runs. Specifically, there remained 52% of the *cis* reactant in the direct irradiation compared with only 81% of the *cis* reactant in the sensitized run.

As a consequence, one would conclude that the dibenzoylstilbene system rearranges predominantly through the singlet excited state.

Attempted Quenching with Naphthalene. It was of interest to check these conclusions by quenching experiments; 0.10 *M* naphthalene together with *cis*-dibenzoylstilbene was used. The concentration of *cis*-dibenzoylstilbene was such that it captured 90% of the incident light. The ratio of product in the direct irradiation to that from one containing 0.10 *M* naphthalene (E_t = 61 kcal/mole) was essentially unity, indicating no quenching. This, on the surface, appeared to be in agreement with the sensitization experiments and also Griffin's[4] report of a lack of *cis–trans* isomerization of piperylenes (E_t = 61 kcal/mole) by dibenzoylethylene. However, the possibility remained that the triplet energy of *cis*-dibenzoylstilbene is lower than 61 kcal/mole, in which case the lack of quenching does not provide additional evidence against triplet-state intervention.[32]

Quenching by Biacetyl. In view of the questions posed above and because an additional probe to test for excited states present during photolysis was desired, it was decided to attempt quenching by biacetyl. In this case, both singlet and triplet quenching are *a priori* possibilities. The singlet of biacetyl is 62 kcal/mole which is lower than the singlets of dibenzoylstilbene (70 kcal/mole) and dibenzoylethylene (72 kcal/mole). Additionally, biacetyl absorbs only very weakly in the regions irradiated.

For quenching experiments with dibenzoylstilbene, a 0.46 *M* solution of biacetyl was found the most practical in that the *cis*-dibenzoylstilbene concentration could be adjusted to capture more than 90% of the incident light. Under these conditions, only 0.17 as much of the *t*-butyl 4-phenoxy-2,3,4-triphenyl-3-butenoate was formed as in unquenched runs. We know from the sensitization results (*vide supra*) that quenching triplets present would not give such a dramatic decrease in efficiency. As noted above, the low singlet energy of biacetyl makes singlet quenching possible. Similar experiments with dibenzoylethylene were not cleanly interpretable since, owing to the low absorption of dibenzoylethylene, conditions could not be found where dibenzoylethylene competed effectively enough with biacetyl for light. Some quenching was observed, however (note Experimental Section).

More evidence on the nature of the biacetyl quenching was desired, requiring further investigation into this system. Biacetyl is one of a few ketones which phosphoresces and fluoresces in solution at room temperature. Several investigators[33–36] have noted this and special significance has been placed on the ratio of phosphorescence to fluorescence intensities. Therefore, the fluorescence and phosphorescence emission of solutions of biacetyl and *cis*-dibenzoylstilbene was investigated under the same and related conditions used for the photolytic work. In the course of these studies it was found that dibenzoylstilbene itself fluoresces with an emission maximum at 400 mμ; biacetyl fluoresces at 480 mμ and phosphoresces in degassed solutions at 520 mμ.

When the exciting light was of wavelength 313 mμ, which is absorbed selectively by the dibenzoylstilbene, quenching of the dibenzoylstilbene fluorescence at 400

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[31] (a) Since *cis–trans* isomerization is seen to be competitive with rearrangement and since this has been reported to go *via* the triplet (*vide supra*), we have evidence that in the ordinary reaction some triplet is formed and that therefore some rearrangement to *t*-butyl 4-phenyl-4-phenoxy-3-butenoate goes *via* the triplet. This cannot exceed 10% however. (b) The conditions were selected to give triplet transfer of at least 90% efficiency in sensitization experiments. (c) One might concern himself in the case of dibenzoylethylene, as one referee has noted, about the possibility that the excited states might be frozen in planar conformations and that the reactive conformations having proximate carbonyl oxygen and phenyl moieties could have a higher extinction coefficient than the predominant nonreactive conformer with close oxygen atoms. This would give the reactive conformer a preference in the direct runs relative to the sensitized runs where it seems likely that transfer will be equally efficient to all molecules in view of the great exothermicity of energy transfer. However, the similarity in n–π^* extinction coefficients for the stereoisomeric dibenzoylethylenes and dibenzoylstyrenes (the dibenzoylstilbenes have the π–π^* tail overlapping) suggests insensitivity of extinction coefficient to geometry and argues against such a factor.

[32] Of course as noted [H. E. Zimmerman and J. S. Swenton, *J. Am. Chem. Soc.*, **86**, 1436 (1964)] lack of quenching in a unimolecular rearrangement does not provide final evidence against a triplet, for some triplet rearrangements are more rapid than even the rate of diffusion.

[33] F. Wilkinson and J. T. Dubois, *J. Chem. Phys.*, **39**, 377 (1963).

[34] H. H. Richtol and A. Beloritt, *ibid.*, **45**, 35 (1966).

[35] J. T. Dubois and B. Stevens, "Luminescence of Organic and Inorganic Molecules," H. P. Kallman and G. M. Spruch, Ed., John Wiley and Sons, Inc., New York, N. Y., 1962, p 115.

[36] H. Okabe and W. A. Noyes, Jr., *J. Am. Chem. Soc.*, **79**, 801 (1957).

mμ was observed. A Stern–Volmer plot is given in Figure 1 and the data in Table II. In such a plot, the reciprocal of fluorescence intensity is linear with the concentration of biacetyl quencher as expected for direct destruction of dibenzoylstilbene singlet molecules by collision with ground-state biacetyl.[37] This provides independent, spectroscopic evidence for singlet quenching as suggested above. In fact, by selecting the concentration of biacetyl used in the photolysis quenching experiments one may obtain the precise extent of singlet quenching from the Stern–Volmer plot. It was found that over 97% of the singlets are quenched. Since 17% reaction persisted with this concentration of biacetyl, it seemed likely that the biacetyl which had accepted energy from dibenzoylstilbene singlet then proceeded, after intersystem crossing to triplet, to triplet sensitize the dibenzoylstilbene and allow the relatively inefficient triplet process to occur. This mechanism is outlined in eq 1–8 of Chart IV and in Figure 2. Thus the levels of biacetyl seem to be "sandwiched" between the dibenzoylstilbene singlet and triplet levels. Further evidence supporting this interpretation is given below.

Table II. Quenching of *cis*-Dibenzoylstilbene Fluorescence[a]

Series	*cis*-Dibenzoylstilbene concn, $M \times 10^3$	Biacetyl concn, $M \times 10^3$	F^0/F
A[b]	3.25	0.00	1.00
		4.65	1.49
		9.30	2.36
B[b]	1.72	0.00	1.00
		3.59	1.14
		7.19	1.55
		10.78	1.95
		14.37	2.31
C[b]	1.72	0.00	1.00
		3.59	1.26
		7.19	1.59
		10.78	1.95
		14.37	2.38
D[c]	0.124	0.00	1.00
		1.80	1.16
		3.60	1.37
		7.20	1.69
		9.00	1.84

[a] Run in 75% benzene, 25% *t*-butyl alcohol. [b] Excitation wavelength 245 mμ. [c] Excitation at 313 mμ.

Chart IV[a]

$$ {}^0\mathrm{D} + h\nu \longrightarrow {}^1\mathrm{D} \quad \text{excitation to singlet} \tag{1}$$

$$ {}^1\mathrm{D} \longrightarrow {}^0\mathrm{D} + h\nu \quad \text{fluorescence} \tag{2}$$

$$ {}^1\mathrm{D} + {}^0\mathrm{B} \longrightarrow {}^1\mathrm{B} + {}^0\mathrm{D} \quad \text{singlet quenching by biacetyl} \tag{3}$$

$$ {}^1\mathrm{B} \longrightarrow {}^3\mathrm{B} \quad \text{biacetyl intersystem crossing} \tag{4}$$

$$ {}^1\mathrm{B} \longrightarrow {}^0\mathrm{B} + h\nu \quad \text{biacetyl fluorescence} \tag{5}$$

$$ {}^3\mathrm{B} \longrightarrow {}^0\mathrm{B} + h\nu \quad \text{biacetyl phosphorescence} \tag{6}$$

$$ {}^0\mathrm{D} + {}^3\mathrm{B} \longrightarrow {}^3\mathrm{D} + {}^0\mathrm{B} \quad \text{biacetyl triplet transfer to } cis\text{-dibenzoylstilbene} \tag{7}$$

$$ {}^3\mathrm{D} \longrightarrow {}^0\mathrm{D} \quad \text{radiationless decay of dibenzoylstilbene triplet} \tag{8}$$

[a] D = *cis*-dibenzoylstilbene; B = biacetyl; 0 and 1 refer to the ground and first excited singlet; and 3 refers to the first excited triplet.

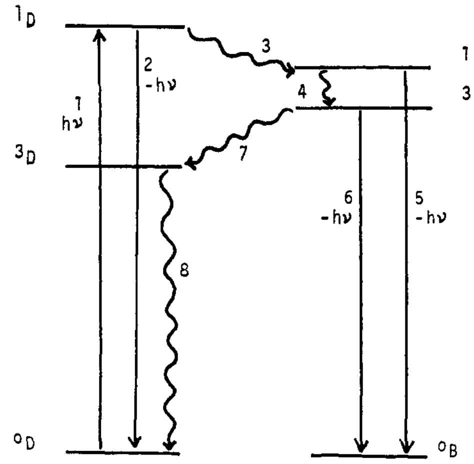

Figure 2. (Note eq 1–8 for definitions.)

From the same type of experiments it was possible to obtain the biacetyl phosphorescence to fluorescence ratio upon excitation of the dibenzoylstilbene. The results are collected in Table III. We note biacetyl fluorescence appears *via* this indirect excitation (*i.e.*, sensitization) while very little biacetyl phosphorescence appears. Normally, in degassed solutions biacetyl fluorescence would be accompanied by phosphorescence, and absence of such emission must mean triplet quenching is occurring.

Table III. Phosphorescence and Fluorescence of Biacetyl with *cis*-Dibenzoylstilbene and *cis*-Dibenzoylethylene Solutions

Run	Biacetyl, *M*	Donor, *M*[a,b]	Exciting wavelength,[c] mμ	*P/F*
1	0.49	0.000	313	8.7
2	0.49	0.000	366	8.7
3[a]	0.49	1.5×10^{-3} [a]	366	0.31
4[a]	0.49	1.5×10^{-3} [a]	434	0.30
5[b]	0.30	5.0×10^{-3} [b]	313	0.70

[a] Dibenzoylstilbene runs. [b] Dibenzoylethylene runs. [c] Biacetyl absorbing in runs 1, 2, and 4 but substituted ethylenes in runs 3 and 5.

To check this interpretation an experiment was run in which biacetyl was excited (at 434 mμ) in the same mixture and again the normal biacetyl phosphorescence was quenched to less than 4% (note Table III), confirming the rationale above.[38]

An interesting question arises as to the reason for the observed large singlet–triplet splitting of the *cis*-dibenzoylstilbene. As stated earlier, n–π* singlet–triplet splitting is generally less than 3000 cm^{-1}. From the above spectroscopic data, the singlet–triplet splitting must be greater than 6000 cm^{-1} or approaching that of π–π* singlet–triplet splitting (*i.e.*, ~10,000 cm^{-1}). One explanation is that the lowest triplet is actually π–π*. This would accord with the less efficient triplet reaction.

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(37) In fact, from the Stern–Volmer plot one can obtain the singlet lifetime of the *cis*-dibenzoylstilbene (τ 9.1 ± 0.9 × 10^{-9} sec).

(38) It is to be noted that such phosphorescence quenching might be interpreted in a manner other than downhill triplet transfer from biacetyl triplet to dibenzoylstilbene. Thus, in the case of singlet destruction, L. M. Stephenson, D. G. Whitten, G. F. Vesley, and G. S. Hammond, *J. Am. Chem. Soc.*, **88**, 3665 (1966), have suggested that energy dissipation can occur by complexation with a higher energy acceptor, complexation facilitating radiationless decay of excited-state species.

Also, the reaction appears to emanate from the *cis* configuration. Interestingly, the triplet may be of the perpendicular variety and thus not conformationally prepared for oxygen attack on phenyl.

In conclusion, the photorearrangements of dibenzoylethylenes appear to originate primarily from the lowest excited singlet. A small fraction (<0.10) in the rearrangement of *cis*-dibenzoylethylene does arise from the triplet configuration. The results thus are in agreement with the feeling of Griffin[4] that phenyl migration in the case of dibenzoylethylene itself probably proceeds by way of the singlet state. The present reaction adds evidence that singlets play an important role in photochemistry. Also we note that this rearrangement provides an excellent example of the proclivity of partially vacant p_y orbitals to attack π systems.

Experimental Section[39]

I. Synthetic, Structural, and Exploratory Aspects. General Techniques. Photolyses were carried out in either of the following two instruments. **Apparatus A.** A Hanovia 450-w, medium-pressure lamp surrounded by a filter sleeve in a quartz-jacketed immersion well was placed in a cylindrical irradiation flask (200 or 1000 ml). Cooling water or filter solution (*vide infra*) was passed through the quartz jacket and maintained at a temperature of 17 ± 3° or 33 ± 4°, respectively.

Filter sleeves consisted of Vycor (cutting off below 220 mμ), Corex (cutting off below 280 mμ), and Pyrex (cutting off below 300 mμ). The filter solution was composed of 40.0 g of copper sulfate pentahydrate, 315.0 g of nickelous sulfate hexahydrate, 600.0 g of cobalt sulfate heptahydrate, and 47.0 g of potassium nitrate dissolved in 1 l. of water. This solution was opaque below 300 mμ; 310 mμ, 1% transmittance (T); 320 mμ, 8% T; 330 mμ, 30% T; 340 mμ, 39% T; 350 mμ, 27% T; 360 mμ, 11% T; 370 mμ, 1% T; and opaque from 380 to 500 mμ.

The irradiation flask was fitted with a nitrogen inlet, a stirring bar, and a capillary gas outlet. The nitrogen stream was either benzophenone ketyl or vanadous ion purified. The stream was monitored for oxygen in an O_2 detector before the immersion well.

Apparatus B. The source, located at the focal point of a parabolic aluminum reflector 13.8 cm long and 14.0 cm in diameter, was a General Electric AH6 high-pressure mercury arc. The light was first filtered by a 2.0-mm Corex D plate (Corning No. 9700) cutting off below 275 mμ (25% T at 275 mμ). Following this was a three-compartment, water-cooled cell which contained filter solutions (*vide infra*). Each compartment was 12.0 cm in diameter and 2.4 cm thick. The sample cell consisted of two 12.0-cm diameter × 5.0 cm path length compartments in series. The faces and partitions between each compartment were quartz plates. The cell was equipped with a Trubore stirrer, nitrogen inlet, and capillary gas outlet, a heat-exchange coil, and a thermistor probe. The cell was maintained at 25.0 ± 0.2°.

Light output was monitored by a phototube between the filter and irradiation cell which served as a check for filter solution decomposition and lamp decay.

Filter solutions[40] were made up as described below. The transmittance curves were measured in a three-compartment cell, each compartment 2.4 cm in length separated by a quartz plate. A 7.2-cm quartz cell containing water served as a reference.

Nickelous sulfate hexahydrate and cobalt sulfate were dissolved in 3.6 *N* sulfuric acid and stannous chloride dihydrate in 7.2 *N* hydrochloric acid. Filter solutions without the use of acid proved somewhat less stable to irradiation.

The properties of filter I were: (neutral) cell 1, 127.0 g/l. of $NiSO_4$; cell 2, 137.0 g/l. of $CoSO_4$; cell 3, 47.0 g/l. of $KC_8H_5O_4$. The potassium hydrogen phthalate was replenished every 30 min. Transmittance was 310–365 mμ, with a maximum at 325 mμ (57% T).

The properties of filter II were: (neutral) cell 1, 127.0 g/l. of $NiSO_4$; cell 2, 137.0 g/l. of $CoSO_4$; cell 3, 29.0 g/l. of $CuSO_4 \cdot 5H_2O$. The filter was transparent in the region from 300 to 365 mμ and transmitted 53% of the light at 327 mμ.

The properties of filter III were: (acidic) cell 1, 90.0 g/l. of $NiSO_4$; cell 2, 200.0 g/l. of $CoSO_4$; cell 3, 10.20 g/l. of $SnCl_2$. This was transparent from 320 to 370 mμ; 320 mμ, 5% T; 330 mμ, 33% T; 340 mμ, 42.5% T; 350 mμ, 31% T; 360 mμ, 12% T; 370 mμ, 1% T; with a maximum at 338 mμ, 43% T.

The properties of filter IV were: (acidic) cell 1, 450.0 g/l. of $NiSO_4$; cell 2, 281.0 g/l. of $CoSO_4$; cell 3, 3.499 g/l. of $SnCl_2$. This solution transmitted light between 310 and 350 mμ; 310 mμ, 5.5% T; 320 mμ, 27% T; 330 mμ, 23% T; 340 mμ, 7.5% T; 350 mμ, 1% T; with a maximum at 323 mμ, 29% T.

The properties of filter V were: (acidic) cell 1, 130.0 g/l. of $NiSO_4$; cell 2, 250.0 g/l. of $CoSO_4$; cell 3, 46.0 g/l. of $SnCl_2$. The filter was transparent from 330 to 360 mμ; 330 mμ, 3% T; 340 mμ, 19.5% T; 350 mμ, 16.5% T; 360 mμ, 4% T; with a maximum at 343 mμ, 21% T.

Solvents and Reagents. Reagent grade benzene was distilled and dried over sodium. Tertiary butyl alcohol was dried over activated molecular sieves and distilled. Reagent grade ethanol (95%) and methanol were used without further purification. Acetophenone was fractionated and the center cut retained. Just prior to use, biacetyl was fractionated and the central cut, bp 24–25° (*ca.* 40 mm), was used. Fractionated cyclohexane was used.

Actinometry. The potassium ferrioxalate actinometer[41] was employed for mechanistic studies. A value of 1.23[41] was used for the quantum efficiency of ferrioxalate over the wavelength range of the filter solutions used.

Liquid–Liquid Partition Chromatography.[42] A two-phase system was made up from 1000 ml of cyclohexane, 400 ml of regent grade dimethylformamide, 250 ml of ethyl acetate, and 30 ml of water. To 700 g of FW80 Celite was added 305 ml of lower phase and this served as the stationary phase.

Preparation of *cis*-Dibenzoylethylene. A solution of 1.50 g (6.34 mmoles) of *trans*-dibenzoylethylene[43] in 750 ml of 95% ethanol was irradiated for 5 hr in apparatus B using filter I. Concentration of the ethanol solution under vacuum at 40° yielded 1.54 g of white needles, mp 125–130°. The infrared and ultraviolet spectra of the material revealed that it was essentially pure *cis*-dibenzoylethylene (lit.[43] mp 134°). Liquid–liquid partition chromatography afforded in the 960–1160-ml fraction 71 mg of a yellow oil and in the 1200–1960-ml fraction 1.41 g (94%) of *trans*-dibenzoylethylene, mp 109–110°. *cis–trans* isomerization on the column was noted.

A second solution of 2.00 g (8.45 mmoles) of *trans*-dibenzoylethylene in 750 ml of 95% ethanol was irradiated for 8 hr under the same conditions as above except that filter II was employed. Concentration of the ethanol solution gave 1.86 g (93%) of crude *cis*-dibenzoylethylene, mp 128–131°. Recrystallization from chloroform–hexane gave 1.78 g, mp 131–132°.

Photochemical Rearrangement of 1,2-Dibenzoylethylene. In a typical irradiation, a solution of 2.10 g (8.88 mmoles) of *trans*-dibenzoylethylene in 900 ml of 95% ethanol was irradiated at 25° under oxygen-free nitrogen for 4.3 hr using apparatus A equipped with the Corex filter.

The oily residue remaining after the removal of the ethanol at 40° *in vacuo* weighed 2.35 g and showed, in its infrared spectrum, hydroxyl absorption at 3.00 μ and strong absorption maxima at 5.81 and 5.98 μ, due to ester and benzoyl carbonyl groups, respectively. The oil was dissolved in ether and bicarbonate extracted. Drying and concentrating the ether fraction gave 2.05 g of neutral material. Acidification and ether extraction of the bicarbonate layer, followed by drying and concentrating the ether, afforded 0.15 g of acidic material. Recrystallization of the "acidic" material from chloroform–hexane afforded 0.14 g (8.8%) of 3-benzoylpropionic acid, mp 117–118°, identified by comparison with an authentic sample (lit.[44] mp 116°).

Liquid–liquid partition chromatographic separation of the neutral portion on a 100 × 4.1 cm column yielded 0.90 g (36%) of ethyl 4-phenyl-4-phenoxy-3-butenoate stereoisomers in the 1000–1120-ml fraction and 0.95 g (52%) of ethyl 3-benzoylpropionate in the 1200–1400-ml fraction. The ethyl 3-benzoylpropionate was purified by molecular distillation at 47–61° (0.14–0.15 mm), to yield 0.82 g of the ester, identified by infrared comparison with an

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[39] All melting points were taken on a hot-stage apparatus and are corrected.

[40] J. S. Swenton, Ph.D. Thesis, University of Wisconsin, 1965. Filter IV corresponds to filter D.

[41] C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc.* (London), **A235**, 518 (1956).

[42] H. E. Zimmerman and D. I. Schuster, *J. Am. Chem. Soc.*, **84**, 4527 (1962).

[43] J. B. Conant and R. E. Lutz, *ibid.*, **45**, 1303 (1923).

[44] N. A. Lange, "Handbook of Chemistry," 9th ed, Handbook Publishers, Sandusky, Ohio, 1956, p 428.

authentic sample prepared by Fischer esterification of 3-benzoylpropionic acid.[6]

Characterization of Ethyl 4-Phenyl-4-phenoxy-3-butenoate. The rearrangement product from the irradiation of dibenzoylethylene was molecularly distilled at 79–82° (0.1 mm) to afford 0.7488 g of colorless oil. The infrared spectrum displayed characteristic absorption maxima in chloroform at 5.80 (ester carbonyl) and 5.95 μ (phenyl enol ether), and was essentially the same as that before distillation. The ultraviolet spectrum (95% EtOH) showed $\lambda_{\max}$ 249 mμ (ϵ 12,800). The nmr spectrum (CCl_4) showed τ 2.4–3.4 multiplet (10 H, aromatic), 4.00 triplet (1 H, J = 6.7 cps, vinyl), 5.90 quartet (2 H, J = 6.8 cps, ethoxyl methylene), 6.78 doublet (2 H, J = 6.7 cps, methylene), and 8.80 triplet (3 H, J = 6.8 cps, ethoxyl methyl). The compound was further purified by gradient-temperature molecular distillation at 95–105° (0.05 mm). Some evidence was available from slightly split nmr peaks that at high conversions the product was a mixture of *cis* and *trans* isomers.

Anal. Calcd for $C_{18}H_{18}O_3$: C, 76.57; H, 6.42. Found: C, 76.22; H, 6.33.

An 81.2-mg portion of the ester was saponified by refluxing for 2 hr in 14 ml of 20% aqueous potassium hydroxide. Acidification, benzene extraction, and concentration yielded 33.7 mg of an oil. A 32.4-mg portion of the oil was subjected to hydrolysis by refluxing in 6 ml of concentrated hydrochloric acid for 8 hr. Some phenol had condensed on the walls of the reflux condenser and was taken up in ether. The aqueous solution was ether extracted; the ethereal extracts were combined and extracted with 5% sodium bicarbonate and 5% sodium carbonate. The bicarbonate extract was acidified giving ultimately 17.2 mg (84%) of 3-benzoylpropionic acid, mp 117–117.5°, from chloroform-pentane. The sodium carbonate extract yielded a total of 13.2 mg (122%) of phenol. The acid was identified from its infrared spectrum and by mixture melting point with an authentic sample. The phenol was characterized as tribromophenol (*vide infra*), mp 91–93°; mixture melting point indicated no depression.

Preparation of *cis*-Dibenzoylstyrene. *cis*-Dibenzoylstyrene was prepared by the base condensation of benzil with acetophenone according to the method of Japp and Klingemann.[45]

Photochemical Rearrangement of *cis*-Dibenzoylstyrene. Irradiation was carried out in apparatus A using the Corex filter sleeve. Dibenzoylstyrene (1.000 g, 3.23 mmoles) was powdered and stirred in 200 ml of 95% ethanol for 2 hr. The resulting solution was irradiated for 2 hr, maintaining a positive oxygen-free nitrogen (*vide supra*) pressure throughout. The solvent was removed under reduced pressure at 50°, yielding 1.091 g of crude material. The infrared spectrum showed a strong band at 5.80 μ (ester carbonyl). The residue was chromatographed on a 2.2 × 100 cm silica gel column, slurry packed in 5% ether–hexane: fractions 1–6, 5% ether–hexane; 7–11, 10% ether–hexane; 12–17, 15% ether–hexane; 18–21, 20% ether–hexane; 24–25, 100% ether; 200-ml fractions were collected to give: fractions 6–12, 0.817 g (71.3%) of ethyl 2,4-diphenyl-4-phenoxycrotonate; 13–16, 0.123 g (12.3%) of *trans*-dibenzoylstyrene; 17–19, 0.069 (6.9%) of *cis*-dibenzoylstyrene; 23–25, 0.145 g (13.8%) of 2,4-diphenyl-4-phenoxycrotonic acid (*vide infra*) identified by infrared. The ethyl 2,4-diphenyl-4-phenoxycrotonate, after molecular distillation at 120° (0.05 mm), showed an infrared spectrum with bands at 5.78, 6.25, 6.70, 7.65, 8.10, 8.40, 8.55, 9.60, and 9.70 μ. The ultraviolet spectrum (EtOH) showed 252 mμ (log ϵ 4.31). The nmr spectrum (CCl_4) showed τ 2.80 multiplet (15 H, aromatic), 3.74 doublet (1 H, vinyl, J = 10 cps), 5.29 doublet (1 H, methine, J = 10 cps), 5.99 quartet (2 H, methylene, J = 7 cps), and 8.99 triplet (3 H, methyl, J = 7 cps).

Anal. Calcd for $C_{24}H_{22}O_3$: C, 80.42; H, 6.19. Found: C, 79.52; 79.43; H, 5.96, 6.08.

Fractions 13–16, after recrystallization from methanol–hexane, melted at 128–129° and had identical infrared and ultraviolet spectra with *trans*-dibenzoylstyrene.[45]

Anal. Calcd for $C_{22}H_{16}O_2$: C, 84.59; H, 5.16. Found: C, 84.33; 84.17; H, 5.12, 5.29.

The *cis*-dibenzoylstyrene was crystallized from ethanol to give material with an infrared spectrum identical with the starting material; a mixture melting point showed no depression.

In a second irradiation of 1.000 g of *cis*-dibenzoylstyrene, a Vycor filter sleeve was used in apparatus A and irradiation was for 3 hr. After 1.5 hr of irradiation, the optical density at 305 mμ had dropped to a nearly constant value. The photolysis solution was concentrated *in vacuo* at 50°, and 0.963 g of brown residue was obtained. This mixture was subjected to liquid–liquid partition chromatography on a 4.5 × 100 cm column filled with 500 g of Celite containing 150 g of lower (stationary) phase; 30-ml fractions were taken. Fractions 30–40 were found to contain 0.335 g (29.1%) of ethyl 2,4-diphenyl-4-phenoxycrotonate; 50–58, 0.151 g (15.1%) of *trans*-dibenzoylstyrene; 59–68, 0.092 g of an unidentified ester; 71–85, 0.216 g (21.6%) of *cis*-dibenzoylstyrene; 86–91, 0.012 g (1.2%) of 2,4-diphenyl-4-phenoxycrotonic acid, mp 137–138°.

In apparatus A using a Corex filter sleeve, 5.000 g of the dibenzoylstyrene in 900 ml of 95% ethanol and 100 ml of tetrahydrofuran was irradiated for 5 hr. The mixture was worked up in the usual manner; 6.746 g of brown residue was chromatographed on silica gel in the same manner as above yielding 64.5% of ethyl 2,4-diphenyl-4-phenoxycrotonate, 15.5% of *trans*-dibenzoylstyrene, 23.3% of 2,4-diphenyl-4-phenoxycrotonic acid (mp 140°), and 8% of an unidentified ester with carbonyl absorption at 5.80 μ. When the ethyl 2,4-diphenyl-4-phenoxycrotonate was subjected to liquid–liquid partition chromatography only one peak was observed. Chromatography of 5.860 g of the ethyl 2,4-diphenyl-4-phenoxycrotonate on a 4.5 × 110 cm silica gel column, slurry packed and eluted with 9% ether–hexane, also gave only one peak. The infrared spectra of adjacent fractions of ethyl 2,4-diphenyl-4-phenoxycrotonate were identical. Thin layer chromatography on silica gel G (according to Stahl) with 50% benzene–chloroform as the mobile phase showed only one spot.

Saponification of Ethyl 2,4-Diphenyl-4-phenoxycrotonate. To 1.146 g (3.2 mmoles) of the ethyl 2,4-diphenyl-4-phenoxycrotonate was added a solution of 0.570 g (1.0 mmole) of potassium hydroxide, 2.0 ml of water, and 9.0 ml of anhydrous methanol. This mixture was refluxed for 4 hr, ether extracted, acidified to pH 3, and ether extracted again. The ethereal layer was dried and concentrated to give 1.120 g of crude acid. Recrystallization from pentane–chloroform afforded 0.868 g (83.5%) of the acid mixture, mp 114–127°. A separation was achieved by cooling the solvent mixture very slowly and separating the crystals mechanically. 2,4-Diphenyl-4-phenoxycrotonic acid melting at 121–123.5° was obtained in 23.6% yield (0.246 g). Further recrystallization from benzene–pentane raised the melting point to 126.0–127.5°.

Anal. Calcd for $C_{22}H_{18}O_3$: C, 79.98; H, 5.49. Found: C, 80.29; H, 5.49.

The ultraviolet spectrum (EtOH) showed 248 mμ (ϵ 13,200). The infrared spectrum ($CHCl_3$) showed 3.30, 3.80, 5.82, 6.03, 6.25, 6.69, 7.70, 8.10, 8.40, 8.57, 9.20, 9.35, and 9.70 μ. The nmr spectrum ($CDCl_3$) showed τ 2.65–3.08 multiplet (15 H, aromatic), 4.21 doublet (1 H, vinyl), and 5.50 doublet (1 H, methine). The other portion of the crystals amounting to 0.393 g (38%), after further recrystallization from benzene–pentane, melted at 141–143°. The nmr, ultraviolet, and infrared spectra were consistent with 2,4-diphenyl-4-phenoxycrotonic acid.

Anal. Calcd for $C_{22}H_{18}O_3$: C, 79.98; H, 5.49. Found: C, 79.87; H, 5.44.

The ultraviolet spectrum (EtOH) showed 254 mμ (ϵ 14,400). The infrared spectrum (KBr) showed 3.25, 3.66, 5.81, 6.05, 6.24, 6.65, 7.60, 8.20, 13.21, 13.57, 14.21, and 14.57 μ. The nmr spectrum ($CDCl_3$) showed τ 2.6–2.9 multiplet (15 H, aromatic), 3.64 doublet (1 H, vinyl), and 5.06 doublet (1 H, methine).

Hydrolysis of the Diastereomeric Acids. A solution of 0.360 g (1.09 mmoles) of 2,4-diphenyl-4-phenoxycrotonic acid (mp 126–127.5°) in 60 ml of concentrated hydrochloric acid was heated to 100° with stirring under nitrogen. A Dry Ice condenser was used in series with a reflux condenser. After 4 hr, the condensers were rinsed with ether, and the ether solution was dried and concentrated using a Vigreux column, giving 0.0576 g (56.2%) of crude phenol. The reaction was stopped after 7 hr, and the acidic solution diluted with water, ether extracted, and this extract dried. The yield after concentration was 0.258 g (93%) of crude 2-phenyl-3-benzoylpropionic acid, mp 143–146°. This was extracted with cold water and then recrystallized from pentane–benzene providing 0.158 g (57%) of acid, mp 151–153°. A mixture melting point with an authentic sample gave no depression, and the infrared and ultraviolet spectra were identical.[7]

The phenolic fraction was dissolved in water and treated with a bromine–potassium bromide solution (*vide infra*) until bromine was no longer consumed. The tribromophenol yield (0.047 g from the ethereal solution and 0.103 g from the aqueous extract) was 0.150 g (35%), mp 87–90°. Recrystallization raised the melting point to 93–94° (lit.[44] 94°). The tribromophenol gave no depression of the melting point with an authentic sample and had an identical infrared spectrum.

Similarly, a solution of 0.500 g (1.51 mmoles) of 2,4-diphenyl-4-crotonic acid, mp 141–142°, in 60 ml of concentrated hydrochloric

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(45) F. R. Japp and F. Klingemann, *J. Chem. Soc.*, **47**, 35 (1885).

acid was heated for 8 hr. After 5 hr, the Dry Ice condenser and the reflux condenser were rinsed with ether, and the ether layer was dried, concentrated, and extracted with 10% potassium hydroxide solution. Acidification with 2 *N* HCl and treatment with bromine–potassium bromide solution (*vide infra*) yielded 0.127 g of crude tribromophenol.

After 8 hr, the reaction mixture was diluted with water and ether extracted, and the ether extract washed with water, dried, and concentrated. The residue was sublimed at 12 mm on a steam bath to a Dry Ice cooled condenser. The 0.0693 g (48.7%) of phenol obtained in this manner was subsequently treated with the bromine–potassium bromide solution (*vide infra*) to precipitate 0.205 g of tribromophenol. The total yield of tribromophenol was 0.332 g (66.7%), mp 92–94°. Identification was made by its infrared spectrum and mixture melting point.

The residue consisted of 0.349 g (91%) of 2-phenyl-3-benzoylpropionic acid which melted after recrystallization at 152.5–153.5° (lit.[7] 152°). A mixture melting point showed no depression.

Synthesis of 2-Phenyl-3-benzoylpropionic Acid. A mixture of 20.0 g (0.103 mole) of phenylsuccinic acid and 78.5 g (1.00 mole) of acetyl chloride was refluxed until the acid dissolved and then for an additional 0.5 hr. The acetyl chloride was then removed *in vacuo* and the product distilled at 190–195° (12 mm) [lit.[46] 204–206° (22 mm)]. The yield was 17.0 g (94%) of a yellow liquid. Crystallization from ether gave colorless needles of phenylsuccinic anhydride, mp 51–53° (lit.[46] 53°).

Phenylmagnesium bromide prepared from 1.20 g (0.05 g-atom) of magnesium and 7.85 g (0.05 mole) of bromobenzene in 40 ml of anhydrous ether was poured through polyethylene tubing packed with glass wool into a dropping funnel. The phenylmagnesium bromide was slowly added with stirring to 8.80 g (0.05 mole) of phenylsuccinic anhydride and the mixture refluxed for 3 hr, allowed to stand overnight, and worked up according to the method of Akhnookh.[7] The crude yield of 2-phenyl-3-benzoylpropionic acid was 2.74 g. After recrystallization the melting point was 153.5–154.5° (lit.[7] 152°). The ultraviolet spectrum (EtOH) showed λ_{max} 242 mμ (ϵ 12,600).

Tetraphenylfuran. The procedure of Berger and Summerbell[47] was adopted.

***cis*-Dibenzoylstilbene.** The procedure of Lutz[48] was applied.

Photolysis of *cis*-Dibenzoylstilbene in Ethanol. The photolysis apparatus A was employed using a Pyrex filter. A solution of 2.000 g (5.15 mmoles) of *cis*-dibenzoylstilbene in 500 ml of benzene and 500 ml of 95% ethanol was purged for 1 hr with oxygen-free nitrogen and then photolyzed for 6 hr. The reaction was monitored by infrared; the carbonyl band of *cis*-dibenzoylstilbene at 6.02 μ decreased in intensity and a new band appeared at 5.78 μ. The ratio of the intensity of the two bands reached 1:3 when the photolysis was stopped.

Concentration of the solution *in vacuo* at 50° yielded 2.20 g of a yellow oil. This was dissolved in ether, extracted with sodium hydroxide, washed with water, dried, and concentrated *in vacuo*. The basic extract yielded less than 25 mg of residue. The remaining oil was dissolved in a minimum amount of chloroform and absolute ethanol added. A white precipitate formed which on further recrystallization gave 0.052 g of *trans*-dibenzoylstilbene, mp 230–231° (lit.[48] 229.7–230.6°). The infrared spectrum was identical with that reported[48] for *trans*-dibenzoylstilbene.

The mother liquors were combined, and the solvent was removed *in vacuo*. The neutral fraction was subjected to liquid–liquid partition chromatography on a 3.5 × 150 cm column in two portions; 40-ml fractions were collected. Fractions 32–35 yielded 47 mg (2.1%) of an oil; 37–40, 1092 mg (49%) of a yellow oil; 42–47, 291 mg (13%) of a yellow oil; 48–51, 53 mg (2.4%) of a yellow-white solid; 52–56, 139 mg (6.3%) of a yellow-white solid; 57–62, 85 mg (4%) of a white solid; 80–90, 76 mg (3.4%) of a colorless oil.

The second peak in the chromatogram showed infrared peaks corresponding to an ester carbonyl (5.78 μ), an aryl ether linkage (7.8–8.2 μ), and the alkyl–oxygen stretching band of an ester (8.2–8.5 μ). The yellow oil (700 mg) was placed on a 70 × 2.5 cm silica gel column, slurry packed in 5% ether–hexane. Fractions of 500 ml were taken: 1–4, hexane; 5–16, 5% ether–hexane. The ester (650 mg) came off in fractions 8–12 as a colorless oil. When placed in cold pentane, 200 mg of white crystals of ethyl 4-phenoxy-2,3,4-triphenyl-3-butenoate formed, mp 100–104°, which were recrystallized from ether–hexane to a constant melting point 104.5–106°. The infrared and nmr of the mother liquors were identical with those of the solid obtained.

The ultraviolet spectrum (cyclohexane) showed λ_{max} 265 mμ (ϵ 13,860). The nmr spectrum (CCl_4) showed τ 2.7–3.0 multiplet (20 H, aromatic), 5.0 singlet (1 H, vinyl), 5.83 quartet (2 H, methylene, J = 7.1 cps), and 8.78 triplet (3 H, methyl, J = 7.1 cps). The infrared spectrum (CCl_4) showed 3.25, 3.28, 3.45, 5.79, 6.27, 6.71, 6.92, 8.23, 8.60, 9.31, 9.40, 9.73, and 14.31 μ.

Anal. Calcd for $C_{30}H_{26}O_3$: C, 82.92; H, 6.03. Found: C, 82.65; H, 6.12.

Fractions 52–56 of the liquid–liquid chromatogram afforded a solid which was obtained in pure form by several crystallizations from benzene, benzene–ethanol, and chloroform–ethanol, mp 217–218° (lit.[48] 220°), and had an infrared spectrum identical with that of *cis*-dibenzoylstilbene reactant. A mixture melting point showed no depression.

Fractions 48–51 gave a white crystalline solid upon crystallization several times from benzene, mp 230–231°. The infrared spectrum was identical with that reported for *trans*-dibenzoylstilbene.[48] A mixture melting point with that isolated by crystallization of the crude photolysis mixture showed no depression.

Photolysis of *cis*-Dibenzoylstilbene in Methanol. Irradiation of 2.00 g of *cis*-dibenzoylstilbene dissolved in 1 l. of 50% benzene–absolute methanol was carried out under the same conditions as the above for 8 hr. The photolysis mixture was worked up in the same manner and the base extract yielded no acidic products.

The neutral fraction was subjected to liquid–liquid partition chromatography taking 40-ml fractions with the following results: fractions 33–36, 118 mg (6.0%) of a yellow oil; fractions 37–38, 186 mg (9.4%) yellow oil; 39–41, 939 mg (47.5%) yellow oil; 42–44 338 mg (17.1%) oil; 48–52, 100 mg (5.1%) off-white solid; 53–56, 189 mg (9.6%) off-white solid; 57–65, 116 mg (5.9%) oil. Fractions 53–56 and fractions 48–52 again corresponded to *cis*- and *trans*-dibenzoylstilbene, respectively, as identified by their infrared spectra, melting points, and mixture melting point. The yellow oil from fractions 39–41 (710 mg) was chromatographed on a 100 × 3.0 cm silica gel column, slurry packed in 5% ether–hexane. Fractions of 500 ml were collected; fractions 1–14 were eluted with 1% ether–hexane; 15–35, 2% ether–hexane; 36–37, 40% ether–hexane. Fractions 1–2 yielded 10 mg of forerun; 3–18, nil; 19–26, 60 mg of an oil, 27–35, 630 mg of the ester as an oil. The oil was crystallized from cold pentane yielding 360 mg, mp 74–77°, and after recrystallization from pentane, 132 mg of solid, mp 75.0–76.5°. The ultraviolet spectrum (EtOH) showed λ_{max} 265 mμ (ϵ 14,000). The nmr spectrum (CCl_4) showed τ 2.7–3.3 multiplet (20 H, aromatic), 4.78 singlet (1 H, methine), and 6.60 singlet (3 H, methoxy). The infrared spectrum (CCl_4) showed 3.28, 3.30, 3.40, 5.75, 6.27, 6.70, 6.92, 6.98, 8.11, 8.27, 8.59, and 14.35 μ.

Acid Hydrolysis of Methyl 2,3,4-Triphenyl-4-phenoxy-3-butenoate. A mixture of 0.525 g (1.25 mmoles) of methyl 2,3,4-triphenyl-4-phenoxy-3-butenoate (mp 77–78°) and 16.5 ml of concentrated hydrochloric acid was refluxed for 8.7 hr with water-cooled and Dry Ice condensers connected in series. The condensers were rinsed with water after 5.0 and 8.7 hr. The aqueous condenser rinses were combined and treated with a solution of 15.0 g of potassium bromide and 10.0 g of bromine in 100 ml of water until the yellow color persisted. The suspension was ether extracted; the ether layer was extracted with 5% sodium bisulfite, washed with water, dried, and concentrated yielding 0.017 g of tribromophenol, mp 83–89°. Recrystallization from ethanol–water gave 10 mg, mp 92–94° (lit.[44] 94°). A mixture melting point with an authentic sample prepared from phenol showed no depression, and infrared spectra (KBr) of the two samples were identical.

The acid hydrolysis mixture was diluted with ice–water and ether extracted, and the combined ether extracts were washed with water and extracted with 10% sodium hydroxide. The basic layer was acidified with 10% hydrochloric acid to congo red (pH 3) and benzene extracted, and the benzene solution was dried and concentrated *in vacuo* yielding 0.104 g of a brown solid residue with a distinct phenolic odor. The residue was triturated with ether to remove the phenol yielding 0.090 g of 2,3-diphenyl-3-benzoylpropionic acid, mp 192–204°. After recrystallization from benzene, 36 mg of the higher melting diastereomer was obtained, mp 208–210°. Infrared, nmr, melting point, and mixture melting point comparisons with an authentic sample prepared independently (*vide infra*) established the structure as 2,3-diphenyl-3-benzoylpropionic acid.[8] The phenol obtained from the trituration was treated with the

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(46) H. Alexander, *Ann. Chem.*, **258**, 75 (1890); A. Spiegel, *ibid.*, **219**, 31 (1883).

(47) D. Berger and R. K. Summerbell, *J. Org. Chem.*, **24**, 1881 (1959).

(48) R. E. Lutz, C. R. Bauer, R. G. Lutz, and J. S. Gillespie *ibid.*, **20** 218 (1955).

brominating solution (*vide supra*) yielding 7 mg of tribromophenol; the total yield of tribromophenol was 24 mg.

The neutral extract from the acid hydrolysis was dried and concentrated yielding 0.373 g of a mixture of esters. The infrared spectrum (CCl_4) showed three carbonyl bands (5.78, 5.80, and 6.01 μ), the 5.78-μ band being attributable to methyl 2,3,4-triphenyl-4-phenoxy-3-butenoate. The mixture was chromatographed on a 70 × 2.5 cm silica gel column, slurry packed in 5% ether–hexane. Fractions of 40 ml were taken; fractions 1–35, hexane; 36–230, 4% ether–hexane; 231–253, 10% ether–hexane; 254–261, ether. Fractions 99–168 gave 0.156 g (42%) of a keto ester with infrared bands at 5.79 and 6.01 μ. The crude solid, mp 125–135°, was recrystallized from methanol yielding 30 mg of the higher melting diastereomer of methyl 2,3-diphenyl-3-benzoylpropionate, mp 164–165° (lit.[8] 160°). Identity was established by infrared, nmr, melting point, and mixture melting point comparisons with an authentic sample (*vide infra*). Fractions 189–270 yielded 0.150 g (40%) of the original ester and fractions 169–180 yielded 0.040 g (10%) of an unidentified product.

The mother liquors from the crystallization of fractions 99–168 were combined and concentrated *in vacuo* yielding 57 mg. This was chromatographed on a 1.5 × 85 cm alumina column (activity IV), slurry packed with hexane. Fractions of 50 ml were taken: fractions 1–8, hexane; 9–37, 5% benzene–hexane; 38–44, 10% benzene–hexane. Fractions 8–12 yielded 0.008 g (14%) of an oil; 13–17, 0.015 g (26%) of a solid, mp 135–148°; 18–19, 0.011 g (19%) of a white solid, mp 141–146°; 20–38, 0.033 g (58%) of a white solid, mp 145.5–148°. Infrared, nmr, melting point, and mixture melting point comparisons with an authentic sample (*vide infra*) established this as the lower melting stereoisomer of methyl 2,3-diphenyl-3-benzoylpropionate.[8]

Synthesis of 2,3-Diphenyl-3-benzoylpropionic Acid.[49] An ether solution of deoxybenzoin (20.3 g, 0.104 mole) and 5.02 g (0.104 mole) of a 50% oil dispersion of sodium hydride was refluxed for 1 hr with an evolution of 3.37 l. of gas (theoretical 2.33 l. of hydrogen). Ethyl bromophenylacetate (20.0 g, 0.082 mole) was added over a 0.5-hr period. The addition was accompanied by evolution of heat and vigorous refluxing. After the addition was completed, the solution was stirred for 1 hr, heated to reflux for 2 hr, and allowed to stand for 12 hr. The ether was removed *in vacuo* and replaced with 75 ml of absolute ethanol and 85 ml of 15% aqueous potassium hydroxide. The solution was refluxed for 3.5 hr, cooled, and diluted with water; 22.3 g (82%) of a white precipitate, a mixture of the diastereomeric 2,3-diphenyl-3-benzoylpropionic acids, was collected. Recrystallization of 10 g of the mixture from benzene gave 1.0 g of the lower melting diastereomer, mp 199–201° (lit.[8] 201°). The remainder of the solvent from the reaction mixture was removed *in vacuo* and 0.231 g of the higher melting diastereomer was isolated, mp 208–211°, after recrystallization from benzene (lit.[8] 211°).

For the higher melting diastereomer the infrared spectrum (KBr) showed 3.0–4.0 (broad), 5.89, 6.00, 6.26, 6.33, 6.70, 6.90, 7.03, 7.70, 7.90, 8.09, 8.32, 8.52, 9.31, 9.70, 9.95, 10.06, 10.72, 13.00, 13.31, 13.67, and 14.2–14.4 μ (broad). The nmr spectrum (acetone) showed τ 1.9–2.2 multiplet (2 H, *o*-benzoyl); 2.3–2.9 multiplet (13 H, aromatic); and 4.20, 4.40, 5.25, and 5.44 AB quartet (2 H, J = 11.5 cps, methine). The calculated chemical shifts are τ_A 4.31 and τ_B 5.34. The infrared, nmr, and melting point were identical with those of the acid isolated from the acid hydrolysis of the photoester (*vide supra*).

For the lower melting diastereomer the infrared spectrum (KBr) showed 3.0–4.0 (broad), 5.89, 5.99, 6.26, 6.70, 6.89, 6.91, 7.08, 7.72, 8.38, 8.45, 9.31, 9.70, 10.15, 10.75, 12.92, 13.38, 13.80, 14.2–14.4 (broad), and 15.26 μ. The nmr spectrum ($CDCl_3$) showed τ −0.59 broad singlet (1 H, acid proton); 1.9–2.2 multiplet (2 H, *o*-benzoyl); 2.5–3.1 multiplet (13 H, aromatic); and 4.78, 4.97, 5.48, and 5.67 AB quartet (2 H, J = 11.0 cps, methine). The calculated chemical shifts are τ_A 4.89 and τ_B 5.56.

Synthesis of the Methyl Esters of 2,3-Diphenyl-3-benzoylpropionic Acid. To 29 ml of anhydrous methanol containing 1.935 g (5.92 mmoles) of the lower melting acid was added 0.50 ml of concentrated sulfuric acid. After refluxing for 1.25 hr this was poured into 150 ml of water and ether extracted, and the ether layer was washed with 5% potassium hydroxide and water. The basic layer was acidified to Congo red (pH 3) and ether extracted, and the ether solution was dried and concentrated *in vacuo* yielding 1.002 g of the diastereomeric acids, mp 199–206°.

The ether solution of neutral components was dried and concentrated *in vacuo*, yielding 0.568 g, mp 143–149°. Recrystallization from methanol gave methyl 2,3-diphenyl-3-benzoylpropionate,[8] mp 147–149°. The infrared spectrum (KBr) showed 3.30, 3.39, 5.79, 5.99, 6.25, 6.33, 6.70, 6.87, 6.90, 6.96, 7.31, 7.46, 7.57, 7.64, 7.71, 7.90, 8.09, 8.35, 8.52, 9.30, 9.90, 10.29, 10.68, 11.70, 12.80, 12.90, 13.30, 13.49, 14.10, 14.35, and 15.01 μ. The nmr spectrum (CCl_4) showed τ 2.0–2.25 multiplet (2 H, *o*-benzoyl); 2.50–3.20 multiplet (13 H, aromatic); 4.86, 5.04, 5.62, and 5.81 AB quartet (2 H, J = 10.5 cps, methines); and 6.40 singlet (3 H, methoxy). The calculated chemical shifts are τ_A 4.96 and τ_B 5.70. By infrared, nmr, and melting point comparisons[8] (*vide supra*), this ester was shown to be identical with that obtained from the degradation.

Esterification of the higher melting acid was accomplished with ethereal diazomethane using Du Pont EXR 101. The solvent was removed and, on cooling, crystals formed and were filtered, yielding 0.160 g of methyl 2,3-diphenyl-3-benzoylpropionate,[8] mp 159–163°. The infrared spectrum (KBr) showed 3.28, 3.31, 3.40, 5.79, 6.00, 6.29, 6.71, 6.90, 7.00, 7.77, 8.61, 8.69, 10.26, 10.68, 12.89, 13.08, 13.26, 13.69, 14.10, 14.41, 14.62, and 15.42 μ. The nmr spectrum ($CDCl_3$) showed τ 2.05–2.30 multiplet (2 H, *o*-benzoyl); 2.35–3.00 multiplet (13 H, aromatic); 4.39, 4.59, 5.25, and 5.45 AB quartet (2 H, J = 11.5 cps, methines); and 6.62 singlet (3 H, methoxy). The chemical shifts were τ_A 4.50 and τ_B 5.34. This ester was shown to be identical with the degradation product (*vide supra*) by infrared, nmr, and melting point comparisons.

II. Mechanistic Aspects. General Procedure. In addition to the purification of solvents as in the preparative irradiations (*vide supra*), fluorometric grade benzene (Matheson Coleman and Bell) was used for fluorescence studies.

Relative product yield determinations were carried out on *cis*-dibenzoylethylene and *cis*-dibenzoylstilbene in the following manner. Ferrioxalate actinometer was used before and after each irradiation to establish that light output remained constant; in some cases a measurement was made in between two portions of a run. Two irradiations were made in each series to determine the relative product formation with and without sensitizer or quencher. Ultraviolet spectra of the photolysis solutions were obtained before and after each irradiation to demonstrate that no inner filter effects were responsible for changes in the product yields. Absorption spectra were run on the filter solutions (*vide supra*) to establish their stability during the irradiation.

Sensitization of *cis*-Dibenzoylethylene. The direct irradiation was carried out in apparatus B using filter combination IV. A solution of 0.968 g (4.15 mmoles) of *cis*-dibenzoylethylene in 150 ml of *t*-butyl alcohol and 600 ml of benzene was irradiated for 4.00 hr. After the actinometer run between irradiations, a second solution of 0.353 g (1.5 mmoles) of *cis*-dibenzoylethylene in 585 ml of benzene, 140 ml of *t*-butyl alcohol, and 25.00 ml (25.20 g, 0.285 *M*) of acetophenone was irradiated for 4.00 hr. The actinometer readings were 2.80, 2.60, and 2.55 mEinsteins/hr. Ultraviolet analysis indicated that acetophenone absorbed 97% of incident light. This calculation used the extinction coefficients at that wavelength where the ratio of acetophenone to reactant absorption was a minimum. The solvent was removed from each solution *in vacuo*. The acetophenone was removed by bulb to Dry Ice cooled bulb vacuum transfer (1.0 mm). The recovered acetophenone (25.17 g, 98%) showed no bands in the infrared and nmr spectra which corresponded to photolysis products or starting dibenzoylethylene. It was further demonstrated (*vide infra*) that the products do not transfer under the above conditions.

The two crude mixtures were each dissolved in 500 ml of benzene, extracted with 5% potassium hydroxide and water, and dried. The basic layer was benzene extracted, acidified with 10% hydrochloric acid to congo red (pH 3), and extracted with ether. The ether layer was dried and concentrated *in vacuo* to give 4-phenoxy-4-phenyl-3-butenoic acid, identified by infrared, direct photolysis, 14.6 mg; sensitized run, 5.6 mg. The remaining neutral benzene solutions were concentrated *in vacuo* and chromatographed by liquid–liquid partition chromatography on a 150 × 3.5 cm column. Fractions of 40 ml were taken; fractions 30–35 gave 0.106 g (0.341 mmole, 8.3%) of an oil; fractions 41–62, 0.821 g (3.50 mmoles, 87%) of a solid. Fractions 41–62 were shown to be *trans*-dibenzoylethylene by the infrared and nmr spectra and melting point.

Fractions 30–35 were identified as *t*-butyl 4-phenoxy-4-phenyl-3-butenoate by the infrared and nmr spectra which were similar to the ethyl ester (*vide supra*). The infrared spectrum ($CHCl_3$) showed 3.35, 5.80, 6.26, 6.71, 6.90, 7.29, 7.30, 8.70, and 14.52 μ. The nmr spectrum (CCl_4) showed τ 2.4–3.3 multiplet (10 H, aromatic); 3.91,

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(49) E. D. Bergman and R. Ikan, *J. Am. Chem. Soc.*, **80**, 3135 (1958).

4.02, and 4.13 triplet (1 H, J = 7.0 cps, vinyl); 6.84 and 6.95 doublet (2 H, J = 7.0 cps, methylene); and 8.61 singlet (9 H, *t*-butyl).

Anal. Calcd for $C_{20}H_{22}O_3$: C, 77.4; H, 7.1. Found: C, 77.1; H, 6.9.

Chromatography of the sensitized photolysis solution gave the following: (40-ml fractions) fractions 31–36 gave 10 mg (0.031 mmole, 2%), fractions 43–62 gave 0.330 g (1.40 mmoles, 95%). The infrared and nmr spectra were consistent with those obtained above.

The ratio of product formation in the sensitized to the unsensitized run was then (0.031 + 0.022)/(0.341 + 0.057) = 0.133. After the correction for maximum light absorbed directly by *cis*-dibenzoylethylene, the ratio was 0.10.

In a second run under the same conditions, a solution of 0.961 g (4.08 mmoles) of *cis*-dibenzoylethylene in 135 ml of *t*-butyl alcohol and 615 ml of benzene was irradiated for 7.0 hr. After the actinometer run between irradiations, a second solution of 0.315 g (1.33 mmoles) of *cis*-dibenzoylethylene in 130 ml of *t*-butyl alcohol, 595 ml of benzene, and 25.00 ml (25.20 g, 0.285 *M*) of acetophenone was irradiated for 7.0 hr. The actinometer readings were 3.25 and 2.82 mEinsteins/hr. Ultraviolet analysis indicated that acetophenone absorbed at least 97% of the incident light. This calculation assumed the extinction coefficients at that wavelength where the ratio of acetophenone to reactant absorption was minimal.

Acetophenone and solvent were removed as above. No acid was detected in either run. Liquid–liquid partition chromatography of the two mixtures on a 3.5 × 150 cm column gave the following results. For the direct irradiation, fractions of 20 ml were taken; fractions 75–83 gave 136.6 mg (0.44 mmole; 10.7%) of the *t*-butyl ester; fractions 102–151 gave 778.2 mg (83%) of *trans*-dibenzoylethylene.

Chromatography of the sensitized photolysis solution gave the following: (20-ml fractions) fractions 90–96 gave 17.6 mg (0.057 mmole; 4.3%) of the *t*-butyl ester; fractions 109–180 gave 287.5 mg (1.21 mmoles; 91.5%) of the *trans*-dibenzoylethylene. The infrared and nmr spectra of the two products were consistent with those obtained above.

The ratio of product formed in the sensitized run to unsensitized run was then (0.057)/(0.44) = 0.129. After correction for maximum light absorbed directly, this ratio was 0.10.

Quenching of *cis*-Dibenzoylethylene with Biacetyl. The irradiations were carried out in apparatus B using filter combination IV. A solution of 7.955 g (33.7 mmoles) of *cis*-dibenzoylethylene in 150 ml of *t*-butyl alcohol and 600 ml of benzene was irradiated for 6.5 hr. After the actinometer run, a second irradiation of 7.988 g (33.8 mmoles) of *cis*-dibenzoylethylene in 560 ml of benzene, 140 ml of *t*-butyl alcohol, and 52.0 ml (0.60 *M*) of biacetyl was carried out for 6.5 hr. The actinometer readings were 3.53, 3.34, 3.05, and 3.11 mEinsteins/hr indicating lamp and filter stability. Ultraviolet analysis of the photolysis solutions showed no inner filter effects had built up and indicated that *cis*-dibenzoylethylene absorbed over 80% of the incident light.

The solutions were concentrated *in vacuo*, and the crude mixtures were each dissolved in benzene, extracted with 5% potassium hydroxide, and dried. The basic layers were acidified to congo red (pH 3) and ether extracted; the ether layer was dried and concentrated *in vacuo* giving: direct run, 30 mg (0.12 mmole, 0.4%) of acid; quenched run, 99 mg (0.39 mole, 1.2%) of acid. The infrared spectrum ($CHCl_3$) of the acid from the direct irradiation showed bands at 2.8–4.1 (broad), 5.90, 6.31, 6.75, 6.94, 7.12, 7.90, 8.61, 9.12, 9.33, 9.80, 9.93, 10.55, and 14.55 μ. The nmr spectrum ($CDCl_3$) showed τ 1.7–2.2 broad singlet (1 H, COOH); 2.3–3.3 multiplet (10 H, aromatic); 3.90, 4.00, and 4.12 triplet (1 H, J = 7.0 cps, vinyl); and 6.60 and 6.71 doublet (2 H, J = 7.0 cps, methylene). The infrared and nmr spectra of the acid from the quenched irradiation were the same as those from the direct except for some impurities which appeared in the former. An estimate of 66% purity based on nmr was attached to the acid obtained from the quenched run. Further attempts at separation were unsuccessful. However, this does provide an upper limit.

From the benzene solution of the neutral portion of the direct run (*vide supra*) 6.047 g of *cis*-dibenzoylethylene was crystallized. Recrystallization from benzene–ethanol gave white needles, mp 110–111°, 4.164 g (52.5%). The mother liquors from the second irradiation were concentrated *in vacuo*, and the residue was chromatographed by liquid–liquid partition chromatography on a 3.5 × 150 cm column. No peaks corresponding to the product ester were found. The mother liquor from the first crystallization was similarly chromatographed taking 40-ml fractions. Fractions 31–36 gave 0.191 g (0.620 mmole, 2.2%) of the *t*-butyl 4-phenoxy-4-phenyl-3-butenoate as verified by infrared and nmr spectra; fractions 40–70 gave 1.507 g of *trans*-dibenzoylethylene. The total recovered *cis*- and *trans*-dibenzoylethylene was 7.554 g (96%). The mass balance for the direct run was 98.6%.

The neutral layer from the quenched run was similarly crystallized, yielding 4.848 g of *cis*-dibenzoylethylene. This was recrystallized and the mother liquor concentrated and chromatographed as above. Again, no peak corresponding to *t*-butyl 4-phenoxy-4-phenyl-3-butenoate was present. The mother liquor from the first crystallization was concentrated *in vacuo* and chromatographed. The chromatogram showed two peaks; 40-ml fractions were taken: fractions 33–37 gave 0.069 g (0.22 mmole; 1.8%) of *t*-butyl 4-phenoxy-4-phenyl-3-butenoate; fractions 42–83 gave 2.581 g of *trans*-dibenzoylethylene. The total yield of *cis*- and *trans*-dibenzoylethylene was 7.429 g (93%). The mass balance from the quenched reaction was 96.3%.

The ratio of product formation in the quenched and unquenched runs was (0.22 + 0.39)/(0.62 + 0.12) = 0.81.

Sensitization of *cis*-Dibenzoylstilbene with Acetophenone. The two irradiations were carried out in apparatus A using the solution filter and a Pyrex filter sleeve. A solution of 0.526 g (1.36 mmoles) of *cis*-dibenzoylstilbene in 750 ml of benzene and 250 ml of *t*-butyl alcohol was irradiated for 40.0 min. After the actinometer measurement between runs, a second irradiation of 0.523 g (1.35 mmoles) in 675 ml of benzene, 225 ml of *t*-butyl alcohol, and 102.3 g (0.85 mole) of acetophenone was carried out for 40.0 min. The actinometer readings were 11 and 10 mEinsteins/hr, indicating lamp and filter stability. The ultraviolet spectra before and after each irradiation of the two photolysis solutions showed no inner filter effects and demonstrated that acetophenone absorbed greater than 85% of the incident light.

The solutions were concentrated *in vacuo*, and the acetophenone was removed by bulb-to-bulb vcuum transfer (*vide supra*). The residues were each dissolved in 500 ml of benzene and extracted with 5% sodium hydroxide and water. The basic layer acidified with 10% hydrochloric acid and benzene extracted, and the benzene was dried and concentrated *in vacuo*. No acid was obtained from either run.

The neutral fraction was chromatographed by liquid–liquid partition chromatography on a 3.5 × 150 cm column, taking 40-ml fractions. Three major peaks were evident from the chromatogram of the direct irradiation: fractions 40–44 gave 99.5 mg (0.215 mmole, 15.8%) of *t*-butyl 2,3,4-triphenyl-4-phenoxy-3-butenoate; fractions 57–63 gave 123.8 mg (0.319 mmole, 24%) of *trans*-dibenzoylstilbene; fractions 64–95 gave 272.2 mg (0.706 mmole, 52%) of *cis*-dibenzoylstilbene. The *cis*- and *trans*-dibenzoylstilbenes were identified by their infrared spectra and melting point. Fractions 40–44 gave the *t*-butyl ester which was identified by its nmr spectrum (CCl_4) which showed maxima at τ 2.70–3.30 multiplet (20 H, aromatic), 4.69 singlet (1 H, methine), and 8.71 singlet (9 H, *t*-butyl). The infrared spectrum (CCl_4) showed 3.28, 3.31, 3.38, 3.42, 5.80, 6.25, 6.71, 6.95, 7.19, 7.30, 8.15, 8.28, 8.71, 9.00, 9.32, and 14.3–14.4 μ.

From the sensitized irradiation, the liquid–liquid scan displayed the same three peaks in the following amounts: fractions 41–45 gave 44.5 mg (0.096 mmole, 7%) of *t*-butyl 2,3,4-triphenyl-4-phenoxy-3-butenoate; fractions 59–65 gave 67.5 mg (0.174 mmole, 13%) of *trans*-dibenzoylstilbene; fractions 66–69 gave 425.1 mg (1.10 mmoles, 81%) of *cis*-dibenzoylstilbene.

The ratio of product formation in the sensitized and unsensitized runs was (0.096)/(0.215) = 0.45. A ratio of 0.29 is left after the correction for light absorbed directly.

Quenching of *cis*-Dibenzoylstilbene with Naphthalene. The two irradiations were carried out in apparatus A using the solution filter and a Pyrex filter sleeve. A solution of 0.520 g (1.34 mmoles) of *cis*-dibenzoylstilbene in 750 ml of benzene and 250 ml of *t*-butyl alcohol was irradiated for 36.0 min. In a second irradiation, 0.524 g (1.35 mmoles) of *cis*-dibenzoylstilbene in 750 ml of benzene, 250 ml of *t*-butyl alcohol, and 12.473 g (0.096 mole) of naphthalene was photolyzed for 36.0 min. The actinometer readings were 34 and 30 mEinsteins/hr indicating lamp and filter solution stability. The ultraviolet spectra before and after each irradiation showed no inner filter effects and established that *cis*-dibenzoylstilbene absorbed 90% of the incident light.

Solvents were removed *in vacuo* and the naphthalene sublimed at 33–35° (0.05 mm) for 4.5 hr. The residues were dissolved in benzene, base extracted, and tested for acid (*vide supra*). No acidic products were found. The benzene solution was concentrated *in vacuo*, and the residues were chromatographed by liquid–liquid partition chromatography on a 3.5 × 150 cm column. Fractions of 20 ml were taken: fractions 69–70 gave 68.5 mg (0.148 mmole, 11%) of *t*-butyl 2,3,4-triphenyl-4-phenoxy-3-butenoate; fractions 86–106 gave 74.6 mg (0.132 mmole, 14%) of *trans*-dibenzoylstilbene; fractions 107–150 gave 316 mg (0.815 mmole, 61%) of *cis*-dibenzoylstilbene. The peaks were identified by nmr and infrared spectra and melting point.

The liquid–liquid partition chromatography of the quenched run on a 3.5 × 150 cm column gave the following: (40-ml fractions) fractions 38–42, 66.1 mg (0.143 mmole, 11%) of *t*-butyl 2,3,4-triphenyl-4-phenoxy-3-butenoate; fractions 53–57, 45 mg (0.115 mmole, 9%) of *trans*-dibenzoylstilbene; fractions 58–100, 382 mg (1.0 mmole, 75%) of *cis*-dibenzoylstilbene.

The ratio of product formation of the quenched to unquenched run was (0.143)/(0.148) = 0.97.

Quenching of *cis*-Dibenzoylstilbene with Biacetyl. The irradiations were carried out in apparatus A using the solution filter and a Pyrex filter sleeve. A solution of 0.501 g (1.29 mmoles) of *cis*-dibenzoylstilbene in 750 ml of benzene and 250 ml of *t*-butyl alcohol was irradiated for 37.5 min. In a second irradiation, 0.506 g (1.30 mmoles) of *cis*-dibenzoylstilbene in 720 ml of benzene, 240 ml of *t*-butyl alcohol, and 40.6 g (0.46 mole) of biacetyl was photolyzed for 37.5 min. The actinometer readings were 0.58 and 0.46 mEinsteins/min, and the ultraviolet spectra of each solution before and after irradiation showed no inner filter effects and showed that *cis*-dibenzoylstilbene absorbed over 90% of the incident light. The solvents were concentrated *in vacuo*, and the residues were each chromatographed by liquid–liquid partition chromatography, 40-ml fractions being taken.

Fractions 37–40 gave 95 mg (0.206 mmole, 16%) of *t*-butyl 2,3,4-triphenyl-4-phenoxy-3-butenoate; fractions 56–62 gave 131 mg (0.330 mmole, 26%) of *trans*-dibenzoylstilbene; fractions 63–104 gave 251 mg (0.620 mmole, 49%) of *cis*-dibenzoylstilbene. In addition, fractions 97–99 contained *ca.* 10 mg of a white solid, mp 192–200°. The compound obtained from several runs (93.2 mg) was chromatographed on a 50 × 2.0 cm silica gel column, slurry packed in 5% ether–hexane. Fractions of 200 ml were taken: fractions 1–4 were eluted with 5% ether–hexane, fractions 5–10 with 10% ether–hexane, fractions 11–34 with 20% ether–hexane. Fractions 12–15 gave 60 mg of 9,10-dibenzoylphenanthrene as a white solid, mp 208–209° (lit.[50] 206°).

The infrared spectrum ($CHCl_3$) showed 3.24–3.30 (br), 6.03, 6.25, 6.31, 6.90, 7.29, 7.53, 7.95–8.35 (br), 8.49, 9.89, 12.11, 14.17, 14.56, and 15.01 (sh) μ. The nmr spectrum ($CDCl_3$) showed τ 1.10–1.30 complex doublet (2 H, aromatic) and 2.12–2.83 complex multiplet (16 H, aromatic).

Anal. Calcd for $C_{28}H_{18}O_2$: C, 87.02; H, 4.69. Found: C, 86.85; H, 4.78.

For the liquid–liquid partition chromatography of the quenched run, 40-ml fractions were taken. Fractions 35–39 gave 16 mg (0.035 mmole, 2.7%) of *t*-butyl 2,3,4-triphenyl-4-phenoxy-3-butenoate; fractions 48–65 gave 97 mg (0.250 mmole, 20%) of *trans*-dibenzoylstilbene; fractions 66–97 gave 351 mg (0.905 mmole, 71%) of *cis*-dibenzoylstilbene.

The ratio of product formation for quenched *vs.* the unquenched runs was (0.035)/(0.206) = 0.170.

Control Experiments. In order to determine whether *t*-butyl 4-phenyl-4-phenoxy-3-butenoate distilled under the conditions in which acetophenone was removed, 190 mg of the ester was vacuum distilled at 45° (0.2 mm) for 2.5 hr in the apparatus described earlier. The ester (186 mg, 98%) remained in the distillation bulb.

In a similar manner, 85.7 mg of *t*-butyl 2,3,4-triphenyl-4-phenoxy-3-butenoate was placed in the same apparatus with 100 ml (102.0 g, 0.85 mole) of acetophenone. The acetophenone was removed at 30° (0.05 mm) over a 4.0-hr period. The residue in the distillation flask was chromatographed by liquid–liquid partition chromatography on a 3.5 × 150 cm column giving one peak. Fractions of 40 ml were taken; fractions 42–47 gave 84 mg (98%) of the ester as verified by nmr and infrared spectra.

Photolysis of *trans*-Dibenzoylethylene. The irradiation was carried out in apparatus B using filter combination IV. A solution of 8.018 g (34.0 mmoles) of *trans*-dibenzoylethylene in 600 ml of benzene and 150 ml of *t*-butyl alcohol was irradiated for 9 hr. The actinometer readings were 3.65 and 3.71 mEinsteins/hr indicating filter and lamp stability. The light input was in excess of three times that necessary for a 2% (220 mg) conversion to *t*-butyl 4-phenyl-4-phenoxy-3-butenoate from the *cis* reactant.

The solution was concentrated *in vacuo* and the residue dissolved in benzene; the benzene was extracted with water, 5% aqueous potassium hydroxide, and water, and dried. The basic layer was acidified with 10% hydrochloric acid to Congo red (pH 3) and extracted with ether, and the ether layer was dried and concentrated *in vacuo* yielding no acidic products. The benzene layer was concentrated *in vacuo*, and the residue obtained was recrystallized from benzene. The mother liquors were combined and concentrated *in vacuo* yielding 3.734 g of solid. This was analyzed for *t*-butyl 4-phenoxy-4-phenyl-3-butenoate by nmr and infrared analysis. No ester was found under conditions where less than 30 mg (1%) could be easily detected by nmr.

Phosphorescence and Fluorescence Studies. All studies were carried out on an Aminco–Kiers spectrophosphorimeter. Degassing was carried out in the usual freeze–pump–thaw cycle at 5.0×10^{-3} mm with oxygen-free nitrogen introduced with every thawing. The samples were periodically checked between freeze–thaw cycles until the emission curve reached a maximum. Generally, ten to twelve cycles were necessary to degas a sample. All joints and stopcocks in the vacuum line and nitrogen train were lubricated with Apiezon "L" grease. The fluorescence studies were carried out without degassing the samples. All biacetyl studies were carried out at room temperature, and the response of the detector was monitored by periodically obtaining traces of a "standard" consisting of a 1 × 1 cm plastic block in which a sample of 9,10-diphenylanthracene was dispersed.

The studies to determine the phosphorescence of *cis*- and *trans*-dibenzoylethylene, *cis*- and *trans*-dibenzoylstyrene, and *cis*- and *trans*-dibenzoylstilbene were carried out in EPA, EA, or CA at 77°K (liquid nitrogen). The EPA solvent was a 5:5:2 mixture of ether, isopentane, and ethyl alcohol by volume; EA was a 1:1 mixture of ether and ethyl alcohol by volume; CA was a 1:1 mixture of chloroform and ethyl alcohol by volume. Samples were purified by several crystallizations and thoroughly dried. Generally, concentrations of 4–30 mg per 1 ml of solvent were employed, and the solvent glasses were checked for impurities. Under the most sensitive instrument settings using the high-speed rotating shutter no phosphorescence could be detected for the above compounds.

Biacetyl Emission and Quenching of Biacetyl Phosphorescence. Studies of biacetyl in deaerated solutions of benzene and benzene–*t*-butyl alcohol were performed at room temperature (*ca.* 28°) utilizing the fluorimeter attachment for the Aminco–Kiers apparatus. The solutions were degassed in the usual manner and allowed to equilibrate to room temperature in the cell compartment of the fluorimeter. The shutter for the exciting radiation remained closed throughout the equilibration as there was a time dependence associated with the fluorescence emission from *cis*-dibenzoylstilbene. No such dependence was observed with biacetyl emission. After approximately 10 min, the shutter was opened and several scans of biacetyl emission were recorded on a Varian scanning recorder. The method of Dubois and Wilkinson[33] was adapted for the study of the emission of biacetyl in the presence of acetophenone. The concentrations of biacetyl and acetophenone were adjusted such that acetophenone captured over 95% of the incident light. The emission observed was that of biacetyl. The ratio of the peak heights of biacetyl phosphorescence to fluorescence (*P*/*F*) were recorded for solutions of biacetyl alone, biacetyl and acetophenone, biacetyl and benzophenone, biacetyl and *cis*-dibenzoylethylene, and biacetyl and *cis*-dibenzoylstilbene. Wavelengths were calibrated with a mercury pen light. The results (Table II) demonstrate that biacetyl triplet is quenched by *cis*-dibenzoylstilbene and *cis*-dibenzoylethylene. The results with benzophenone and acetophenone are consistent with those of Dubois and Wilkinson.[33]

Quenching of *cis*-Dibenzoylstilbene Fluorescence. In addition to the two biacetyl emission bands at 480 and 520 mμ, a third emission was noted at 420 mμ at biacetyl concentrations less than 0.3 *M*. Concentrations of biacetyl were varied as were the exciting wavelengths in two series of experiments. Table II gives the experimental conditions and results of these studies. A Stern–Volmer relationship was followed and a plot of F^0/F *vs.* biacetyl concentration is depicted in Figure 1.

To establish the source of the 420-mμ band, the *cis*-dibenzoylstilbene was recrystallized, and the emission spectra were rerun. Associated with this band was a time-dependent increase under continuous excitation. Therefore, all measurements reported above were taken at zero time utilizing the shutter technique (*vide supra*).

Several experiments were initiated to determine the origin of the time dependence of the 420-mμ band. Emission was observed

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(50) W. Dilthey, S. Henkels, and M. Leonhard, *J. Prakt. Chem.*, **151**, 97 (1938).

from the *trans*-dibenzoylstilbene in the same region as *cis*-dibenzoylstilbene (*ca.* 410 mμ) and also displayed the same time dependence though it initially decreased in intensity, then began the increase in the same manner as the *cis* isomer. When a study on the emission of the product ester was made, the emission again appeared in the same region (*ca.* 420 mμ) and appeared as a very intense band. These results strongly indicate though do not prove that this time dependence occurs from the *cis–trans* isomerization and is enhanced further by product formation. To minimize these effects, the Stern–Volmer studies were carried out using the narrowest slits possible for the exciting light.

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Intermediates in the Photochemical Rearrangements of Bicyclo[3.1.0]hexenones[1,2]

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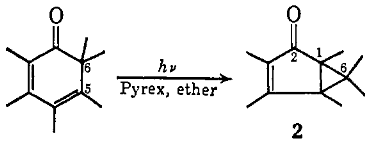
Abstract: Photolysis of hexamethylbicyclo[3.1.0]hexenone (**2**) in methanol through Pyrex gave the crystalline methoxyenol **4**, considered to result from the trapping of a dipolar intermediate (B) by the solvent. The photolysis can be sensitized by benzophenone. Compound **4** loses methanol thermally or in acid, giving the enolic triene **5** which, on further treatment with acid, gives hexamethyl-2,5-cyclohexadienone (**3**). The latter was synthesized independently by the acid-catalyzed rearrangement of hexamethyl-2,4-cyclohexadienone (**1**). The course of these photochemical and acid-catalyzed rearrangements was verified using **2** variously labeled in the methyl groups (as CD_3). The photoproduct **4** could be converted by base to its keto form **17**, which underwent thermal elimination of methanol to produce the dienone **18**. Thermal isomerization of enol **5** gave its keto form **19**, isomeric with **18**. The implication of these results for the photolysis of bicyclo[3.1.0]hexenones and the tendency to form 1,4- (rather than 1,3-) cyclohexadienes in ground-state reactions are discussed.

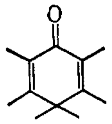
Isomerization of hexamethyl-2,4-cyclohexadienone (**1**) on irradiation in ether through Pyrex afforded the bicyclo[3.1.0]hex-3-ene-2-one **2** in excellent yield.[3]



1 **2**

This reaction, which represents a departure from the usual photochemical behavior of 2,4-cyclohexadienones,[4] proceeds *via* a "bond-crossing," rather than alkyl migration mechanism (*i.e.*, carbons 6 and 5 in **1** become respectively carbons 6 and 1 in **2**).[3]

In a study of solvent effects on the transformation **1** → **2**, it was observed[5] that the reaction proceeded more rapidly in ethanol than in ether; for example, conversions requiring about 5 hr in ether required (all other conditions being the same) only 0.5–1.0 hr in ethanol. However, **2** underwent further photoisomerization in this solvent, and work-up after irradiation for 3 hr led to the isolation of cross-conjugated dienone **3** in excellent yield.[5] Although a few photoisomerizations of bicyclo[3.1.0]hexenones to 2,5-cyclohexadienones are known,[6,7] this result seemed rather strange because the reverse path is much more common,[8] and indeed we have observed (*vide infra*) the photochemical conversion of **3** → **2** in ether.



3

Accordingly, we undertook a careful study of the photolysis of **2** in methanol (chosen in preference to ethanol, to simplify the nmr spectra). In this paper we show that **3** is *not* a direct photoproduct of **2**, but is formed from the photoproduct by thermal and/or acid-catalyzed rearrangements. The photoproduct is shown to have the enolic structure **4**, and probably arises from reaction of a dipolar intermediate with a mole of the solvent. The general significance of these results for the various observed photochemical reactions of bicyclo[3.1.0]hexenones is discussed.

Results

Bicyclo[3.1.0]hexenone **2** was irradiated through Pyrex in methanol, the photolysis being monitored by the change in ultraviolet absorption spectrum. In order to prevent the photoproduct from being converted to **3** by acid-catalyzed reactions, all apparatus was washed

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(3) H. Hart, P. M. Collins, and A. J. Waring, *J. Am. Chem. Soc.*, **88**, 1005 (1966).

(4) For a recent review, see G. Quinkert, *Angew. Chem. Intern. Ed. Engl.*, 4, 211 (1965).

(5) We are indebted to Dr. Richard M. Lange, National Science Foundation Postdoctoral Fellow, 1964–1965, for these initial observations. Dr. Lange was also the first to isolate and characterize the 2,5-dienone 3.

(6) D. H. R. Barton and W. C. Taylor, *J. Chem. Soc.*, 2500 (1958).

(7) D. I. Schuster and A. C. Fabian, *Tetrahedron Letters*, 4093 (1966).

(8) For a review, see O. L. Chapman, *Advan. Photochem.*, 1, 323 (1963).