The numbering for the two styryl moieties in the perpendicular species was taken as 1 (β-styryl); 2 (α-styryl); 3 (carbon bearing the ethynyl group); 4,8 (*ortho*); 5,7 (*meta*); 6 (*para*) in the first styryl group and 9 (β); 10 (α); 11; 12, 16 (*ortho*); 13, 15 (*meta*); 14 (*para*). Semiempirical AO repulsion integrals were taken as (in electron volts; AO's given in parentheses) (1,1), 10.53; (1,2), 7.68; (1,3), 5.15; (1,4), 3.95; (1,9), 7.39; (1,10), 9.39; (1,12), 5.51; (1,13), 3.77; (1,14), 3.35; (2,8), 5.43; (3,4), 7.28; (3,5), 5.44; (3,6), 4.88; (3,10), 5.13; (3,11), 3.49; (4,11), 2.91; (4,16), 2.51; (5,10), 2.91; (5,11), 2.29; (5,15), 1.71; (5,16), 2.04; (6,10), 2.63; (6,11), 2.10; (6,14), 1.50; (6,15), 1.60; and (6,16), 1.88.

The values of the multicenter integrals used when differential overlap at the acetylenic carbon atoms is included are (in electron volts) (1,1,1,2), 3.26; (1,2,1,2), 1.33; (1,9,1,9), 0.07; (1,1,10,9), 2.98; (1,9,10,2), 0.07; (1,12,10,9), 1.19; (1,10, 1,10), 0.57; (1,10,2,9), 0.14; and (1,10,1,9), 0.14.

Φ_1 and Φ_2 are the two lowest configurations of the radical anion with the odd electron in ψ_9 and ψ_{10}, respectively. The off-diagonal matrix element, F_{12}, between these two configurations is given below. This is zero even if differential overlap of the acetylenic carbon atoms is included, since each of the molecular orbital repulsion and exchange integrals is zero.

$$F_{12} = \int \Phi_1 F \Phi_2 \mathrm{d}\tau = 2\sum_{1}^{8} G_{k9k10}{}^{\mathrm{MO}} - \sum_{1}^{8} G_{k910k}{}^{\mathrm{MO}} = 0 \qquad (4)$$

Relative to the energy of the lowest triplet configuration of the dianion Φ_5, the energy of the two singlet configurations, Φ_3 and Φ_4 (two electrons in ψ_9 and ψ_{10}, respectively), is

$$G_{10,10,10,10}{}^{\mathrm{MO}} - G_{9,10,9,10}{}^{\mathrm{MO}} + G_{9,10,10,9}{}^{\mathrm{MO}} = 2.124 \text{ eV} \qquad (5)$$

The off-diagonal matrix element, F_{34}, between the configurations Φ_3 and Φ_4 with differential overlap included is

$$F_{34} = \int \Phi_3 F \Phi_4 \mathrm{d}\tau = G_{9,10,10,9}{}^{\mathrm{MO}} = 0.0089 \text{ eV} \qquad (6)$$

The energy of the lower state upon mixing is 2.11 eV above the energy of the lowest triplet configuration.

Acknowledgment. We acknowledge with pleasure support of this research by the U.S. Army Research Office (Durham) and a National Institutes of Health Predoctoral Fellowship to J. R. D.

Singlet–Triplet Differentiation and Dibenzoylethylene Photochemistry. Mechanistic and Exploratory Organic Photochemistry. LIX[1]

Howard E. Zimmerman and V. Joseph Hull[2]

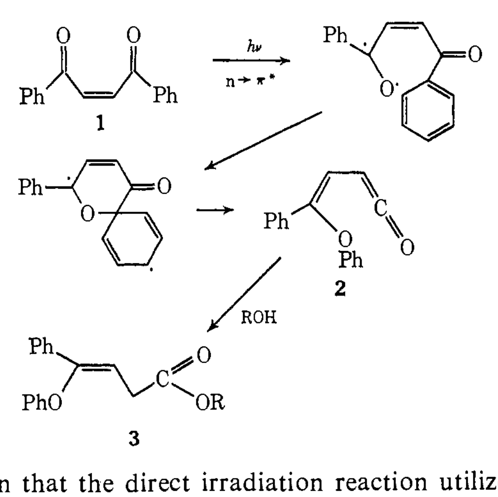
Contribution from the Chemistry Department of the University of Wisconsin, Madison, Wisconsin 53706. *Received March 30, 1970*

Abstract: The photochemistry of dibenzoylethylene is frequently quoted as a classic case where direct irradiation gives a rearrangement product and photosensitization with benzophenone in 2-propanol affords dibenzoylethane. The conclusion usually drawn is that the product of direct irradiation must therefore be derived from the singlet excited state and the product arising on use of benzophenone can therefore be assumed to come from the triplet. The present paper provides evidence that this textbook example has been oversimplified. Instead, the reduction product, dibenzoylethane, has now been shown to result from hydrogen transfer from solvent to dibenzoylethylene by triplet benzophenone. Methods are presently provided to differentiate between energy transfer and chemical intervention of the sensitizer. One test relies on the use of nonhydrogen abstracting sensitizers and the other depends on knowledge of the lifetime of the sensitizers employed.

Previously we reported the rearrangement of dibenzoylethylene to esters of 4-phenyl-4-phenoxy-3-butenoic acid on photolysis in alcoholic solvents[3] (note Chart I). We also noted the generality of the transformation and reported an unusual selectivity in the case of dibenzoylstyrene wherein only one of two possible migrations occurred.[3] The dibenzoylethylene example was independently uncovered by Griffin.[4]

Also, we found that acetophenone sensitization in *t*-butyl alcohol gave rise to the same rearrangement, however, with lower quantum efficiency ($\Phi = 0.0034$) than in the direct irradiations ($\Phi = 0.037$). It was our conclusion that the direct irradiation reaction utilized the

Chart I



---

[1] For paper LVIII, see H. E. Zimmerman, D. F. Juers, J. M. McCall, and B. Schröder, *J. Amer. Chem. Soc.*, **92**, 3474 (1970).

[2] NSF Graduate Fellow, 1965–1969.

[3] H. E. Zimmerman, H. G. Dürr, R. S. Givens, and R. G. Lewis, *ibid.*, **89**, 1863 (1967); H. E. Zimmerman, H. G. Dürr, R. G. Lewis, and S. Bram, *ibid.*, **84**, 4149 (1962).

[4] G. W. Griffin and E. J. O'Connell, *ibid.*, **82**, 4148 (1962).

Table I. Photosensitized Runs Using Triphenylene

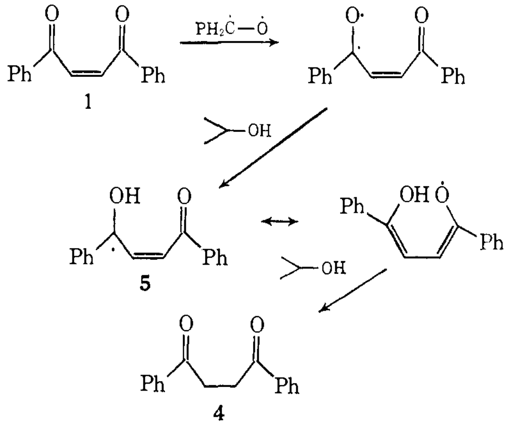
Run[a]	Triphenylene, M	Dibenzoylethylene, M	Sensitizer light capture, %[b]	Max singlet transfer, %[b]	Φ triplet rearr[c]	Φ reductn
T1[d]	0.0043	0.000520	83	11.5	0 (0.005)	<0.0004
T2[d]	0.0045	0.000248	92.5	5.5	0.001 (0.0047)	<0.001
T3[e]	0.022	0.000293	98	6.5	0.0039 (0.0068)	

[a] Irradiating wavelength 300–360 nm. [b] Calculated; see Experimental Section. [c] Corrected for maximum yields from direct absorption and singlet sensitization; values in parentheses are uncorrected. [d] 2-Propanol solvent. [e] 2:1 2-propanol–benzene solvent.

singlet excited state primarily and that the triplet, when generated, would rearrange, although reluctantly.

A very interesting observation reported by Griffin[4] was that irradiation with benzophenone in 2-propanol led to double bond reduction affording dibenzoylethane. The most obvious interpretation was that the direct irradiation generated the singlet which rearranged while the benzophenone run involved the triplet of dibenzoylethylene which abstracted hydrogen from the solvent, leading to dibenzoylethane (note Chart II). However, Griffin[4] suggested caution in interpreting these results as demonstrating multiplicity.

Chart II



Less cautiously, a number of textbooks and review articles have concluded that the difference in product, with and without added sensitizer, derives from a differerence in multiplicity of the reacting species and that such a difference can be used to demonstrate the involvement of more than one excited state. The reaction has become a classic example demonstrating singlet–triplet differentiation.

However, in view of our own findings (*vide supra*) that in *t*-butyl alcohol no reduction product was formed and that the ordinary rearrangement occurred, we thought it wise to investigate the dibenzoylethylene reaction further.

The present investigation employed two approaches. In one, we studied the photochemical behavior of dibenzoylethylene triplet in 2-propanol, with the triplet generated by nonhydrogen-abstracting sensitizer.

In the other mode of attack on the problem, the photochemistry of dibenzoylethylene and benzophenone in 2-propanol was scrutinized under conditions where benzophenone triplet molecules would not have sufficient lifetime to collide with and transfer energy to dibenzoylethylene.

Results

Direct Irradiations. Although we have previously studied the rearrangement reaction[3] in ethanol and also *t*-butyl alcohol, it appeared necessary for control purposes to have direct irradiations in 2-propanol. These photolyses revealed that the usual dibenzoylethylene rearrangement occurred, however, in this case to give the 2-propyl ester **3** (R = 2-propyl). Actinometric runs afforded a quantum yield of 0.030.

Sensitization With Triphenylene. Runs using triphenylene as sensitizer in 2-propanol solvent were made with the idea of determining the amount of reduction of dibenzoylethylene which would occur where the sensitizer did not present complications as a result of its own hydrogen-abstracting ability, as in the case of benzophenone. Triphenylene has a triplet energy high enough (E_T = 66.6 kcal/mol)[5a] to excite dibenzoylethylene ($E_T < 61$ kcal/mol)[3] to its triplet and thus was a reasonable choice. Triphenylene, however, presents two experimental difficulties. The first is its limited solubility in 2-propanol (*ca.* 4.5×10^{-3} M) which allows considerable direct light capture by the dibenzoylethylene. This problem was avoided in one run by using a 2:1 mixture of 2-propanol–benzene in which triphenylene was much more soluble. The second difficulty is that triphenylene, although it has a high intersystem crossing efficiency ($\phi_{ic} = 0.95$),[5b] has a long singlet lifetime ($\tau_{\text{fluorescence}} = 36.6$ nsec)[5b] and thus the singlet is capable of delivering energy before intersystem crossing occurs unless low concentrations of acceptor are used. In all triphenylene runs the amount of possible singlet sensitization was calculated from the singlet lifetime and the rate of diffusion in 2-propanol (from the Debye equation[6]). The triphenylene runs are summarized in Table I.

It may be seen that in the triphenylene runs there is some rearrangement, which may be accounted for as deriving from both the singlet and the triplet. In the runs in 2-propanol solvent the amount of rearrangement from direct light absorption by the dibenzoylethylene and singlet transfer from the sensitizer is great enough to obscure largely the reaction from the triplet. In 2-propanol–benzene solvent the presence of rearrangement deriving from triplet sensitization may be clearly observed. No dibenzoylethane was observed in any of the runs; the maximum quantum yields for dibenzoylethane formation given in the table are based on unaccounted-for material. Additionallly, it should be

---

(5) (a) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," Wiley, New York, N. Y., 1967, p 298; (b) I. B. Berlman, "Handbook of Fluorescence Spectra of Aromatic Molecules," Academic Press, New York, N. Y., 1965, p 171.

(6) P. Debye, *Trans. Electrochem. Soc.*, **82**, 265 (1942).

noted that *cis–trans* isomerization of reactant dibenzoylethylene was observed as in the earlier study.[3]

Studies with Benzophenone Sensitization and Varying Dibenzoylethylene Concentration. At this point the evidence, as a result of the triphenylene studies, was against the triplet of dibenzoylethylene being the entity leading to dibenzoylethane. An approach which promised to provide independent evidence was the utilization of dibenzoylethylene at increasingly more dilute concentrations in benzophenone-sensitized runs. The question was whether the reduction would persist beyond that point where triplet energy transfer to dibenzoylethylene was significant. The results of these runs are listed in Table II.

Table II. Runs with Benzophenone Present and Varying Dibenzoylethylene Concentrations

Run[a]	Benzophenone, *M*	Dibenzoylethylene, *M*	Conversion, %	% triplet transfer[b]	Φ reductn
B1	0.073	0.00202	10	28	0.016
B2	0.043	0.000500	27	8.7	0.007
B3	0.076	0.000451	35	7.9	0.017
B4	0.044	0.000352	25	6.3	0.028
B5	0.045	0.000316	21	5.7	0.019

[a] Irradiating light 300–360 nm. [b] See text.

The per cent triplet transfer is useful here in estimating the relative amounts of triplet energy transfer and hydrogen abstraction to be expected from the benzophenone triplets, and is calculated from the rates for these processes. These rates have been studied in 2-propanol by several groups of workers.[7]

The rate of hydrogen abstraction from 2-propanol by benzophenone triplets is

$$\frac{-\mathrm{d}[^3\mathrm{B}]}{\mathrm{d}t} = k_{\mathrm{abstr}}[\text{2-propanol}][^3\mathrm{B}] = (1.28 \times 10^6)(13.1)[^3\mathrm{B}] = 1.68 \times 10^7[^3\mathrm{B}]$$

Similarly, the rate of triplet energy transfer is

$$\frac{-\mathrm{d}[^3\mathrm{B}]}{\mathrm{d}t} = k_{\mathrm{diff}}[\mathrm{E}][^3\mathrm{B}] = 3.2 \times 10^9[\mathrm{E}][^3\mathrm{B}]$$

where k_{diff} is calculated from the Debye equation[6] and [E] is the concentration of dibenzoylethylene. Hence, the ratio of hydrogen abstraction to triplet transfer is

$$R = \frac{1.68 \times 10^7}{3.2 \times 10^9[\mathrm{E}]}$$

and triplet transfer as a percentage of all benzophenone triplets is

$$\text{per cent triplet transfer} = \frac{1}{1 + R} \times 100$$

The lack of rearrangement observed in the benzophenone-sensitized runs may serve as confirmation of the effectiveness of the "per cent triplet" as a safety factor in preventing sensitization by the benzophenone. With the per cent triplet transfer expected, the low quantum yield of rearrangement for the triplet, and the light outputs employed in these studies, the amount of rearrangement product formed should have been small enough to escape detection. Indeed, no rearrangement product was observed.

The use of benzophenone as a sensitizer for dibenzoylethylene presented experimental difficulties in that both dibenzoylethylene and dibenzoylethane tended to cocrystallize from solution along with benzophenone, and in addition dibenzoylethylene partially sublimed together with benzophenone. In the present experiments the benzophenone and dibenzoylethylene were sublimed from the photolysis mixtures and the residues were chromatographed. These experimental difficulties limited accuracy and led to some scatter in obtaining quantum yields for photoreduction. However, it should be noted that over the range of concentrations employed there is no apparent trend in the quantum yields, and in particular there is no diminution of quantum yields as lower concentrations are attained.

Interpretative Discussion

The first point meriting attention is the very similar quantum yield obtained in the present 2-propanol irradiation ($\Phi = 0.030$) compared with our earlier studies in *t*-butyl alcohol ($\Phi = 0.037$); this similarity occurs despite slight differences in solvent and is consistent with the reaction mechanism given in eq 1, since the efficiency of the reaction is determined in the rearrangement portion of the process and is independent of the subsequent dark reaction of ketene **2**.

The observation of formation of dibenzoylethane on irradiation with benzophenone would ordinarily be interpreted as sensitization of dibenzoylethylene to form T_1 followed by reaction of T_1 to give reduction product. However, the evidence of continued formation of dibenzoylethane under conditions where the concentration of dibenzoylethylene is too low to permit appreciable triplet energy transfer clearly shows that some mechanism other than energy transfer must be occurring. Thus, the quantum yield of dibenzoylethane formation remains in the range $\Phi = 0.018 \pm 0.008$ in the photolyses summarized in Table II. Here the concentration of dibenzoylethylene ranged from 2.20×10^{-3} to 3.16×10^{-4} *M*. Over this concentration range the per cent triplet transfer occurring from the benzophenone triplets being generated ranged from 5.7 to 28 (note Results). From this, two things are apparent. First, reduction is occurring at a steady level despite a fivefold change in triplet transfer. Second, in the run where the per cent triplet transfer is only 5.7, the quantum yield for triplet reaction to form the reduction product would have to be 0.35. This value is clearly discordant with the triphenylene-sensitized runs where no reduction is observed despite an expected triplet energy transfer of 70–90%.

Hence, the evidence rules out triplet dibenzoylethylene as the species responsible for dibenzoylethane formation and points to a species of much longer lifetime which will be able to diffuse to dibenzoylethylene even at the very low concentrations employed.

The triphenylene sensitization studies independently lead to the same conclusion that the triplet of dibenzoyl-

---

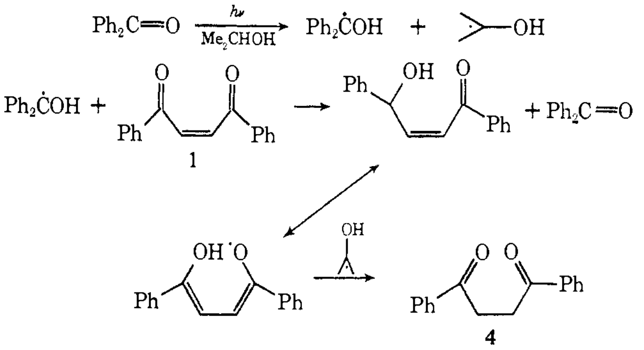
(7) (a) A. Beckett and G. Porter, *Trans. Faraday Soc.*, **59**, 2038 (1963); (b) S. G. Cohen, D. A. Laufer, and V. Sherman, *J. Amer. Chem. Soc.*, **86**, 3060 (1964).

ethylene is not reacting to form dibenzoylethane. With formation of dibenzoylethylene triplet by triphenylene sensitization and the observation of only the ordinary dibenzoylethylene rearrangement, the behavior of the triplet can be considered as defined. This behavior does not include reduction to dibenzoylethane, much less to the extent of a quantum yield of 0.35 as would be required by the benzophenone studies if the triplet did reduce.

Accordingly, we are now left with the need for a different mechanism for the photoreduction in the presence of benzophenone. When one considers the photochemistry of benzophenone in 2-propanol, it is clear that the hydroxybenzhydryl radical is readily generated and that this radical is an excellent hydrogen donor. There is precedent for hydrogen donation from this radical species to hydrogen acceptors. Photochemically generated hydroxybenzhydryl radicals have been shown to be hydrogen transfer agents in the reduction of acridine,[8] aryl-N-alkylimines,[9] and various azo dyes.[10-12] Hydroxybenzhydryl radicals generated thermally from the decomposition of benzopinacol have been shown to give reduction of imines[6] and cyclopropyl ketones.[13]

In the case of dibenzoylethylene, hydrogen transfer by the hydroxybenzhydryl radical to one of the carbonyl oxygens leads to a species which can pick up a second hydrogen either from solvent, from a second hydroxybenzhydryl radical, or most likely from the hydroxyisopropyl radical initially engendered by the triplet benzophenone hydrogen abstraction. This mechanism is given in Chart III.

Chart III



One additional conclusion is possible from the triphenylene results. Since no dibenzoylethane is observed on triphenylene sensitization, and yet hydrogen abstraction from solvent by dibenzoylethylene triplet is an *a priori* possibility, one can conclude that the rate of hydrogen abstraction by dibenzoylethylene triplet is slow relative to the rate of dibenzoylethylene (triplet) rearrangement.

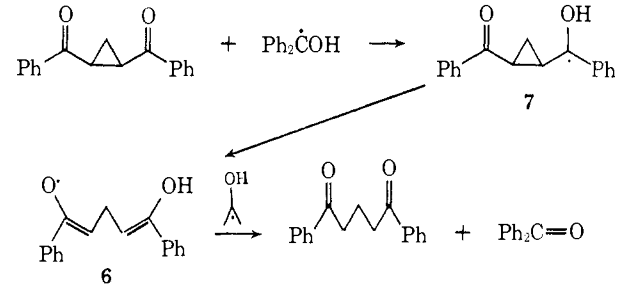
But even the preferred triplet reaction, namely rearrangement, is inefficient. The observation of a considerably lower quantum yield for dibenzoylethylene in the sensitized irradiation compared with the direct one in *t*-butyl alcohol[3] must derive either from a more rapid rate of rearrangement for the singlet excited state or a more rapid rate of excited state decay for the triplet. Pertinent to this is the knowledge[3] that direct and sensitized irradiations lead to *cis–trans* isomerization of dibenzoylethylene competitive with the rearrangement. This accounts for energy dissipation in both types of runs and for the less than efficient quantum yields. There is no *a priori* reason for assuming that the *cis–trans* isomerization will be equally efficient for singlets and triplets, and the possibility of an increased rate of triplet decay, here by geometric isomerization, is real.

Finally, we note that hydrogen transfer from protonated ketyl radicals, such as hydroxybenzhydryl, is a modestly common and general reaction and may account for many of the reductions of π systems observed photochemically.[14]

Accordingly, the formation of saturated ketones from the photolysis of unsaturated ketones may derive from hydrogen abstraction by a ketone present, reactant or product, and delivery of a proton to the π system being reduced.

One example is very similar to the present study and that is the observed photochemistry of dibenzoylcyclopropane where again direct irradiation in 2-propanol gave a *cis–trans* isomerization and benzophenone-sensitized irradiation gave the ring-opened reaction product, 1,5-diphenyl-1,5-pentanedione.[11b] With our present results in hand and the knowledge[13] that hydroxybenzhydryl radical, generated nonphotochemically, can reduce cyclopropyl ketones, we can hypothesize (note Chart IV) that the effect of benzophenone sensitizer again is to deliver hydrogen rather than to afford triplet. Hence the question of whether stereoisomerization derives from the singlet or triplet still remains open.

Chart IV



In conclusion, we repeat the caution that excited state multiplicities cannot safely be determined on the basis of single sensitization or quenching experiments.

Experimental Section[15]

Photolysis Apparatus. The "black box" photolysis apparatus, described in detail earlier as apparatus B,[3] used a General Electric AH6 mercury arc in a deep parabolic reflector. The 12-cm beam was filtered through a 2.0 mm Corex D plate (Corning No. 9700) and through a three-compartment, water-cooled solution filter (*vide infra*). The sample cell was maintained at 25 ± 0.2° and

---

[8] E. Vander Donckt and G. Porter, *J. Chem. Phys.*, **46**, 1173 (1968).

[9] A. Padwa, W. Bergmark, and D. Pashayan, *J. Amer. Chem. Soc.*, **91**, 2653 (1969).

[10] W. F. Smith, Jr., and B. W. Rossiter, *ibid.*, **89**, 717 (1967).

[11] G. Pacifici and G. Irick, Jr., *Tetrahedron Lett.*, 2207 (1969).

[12] H. C. A. van Beek, P. M. Heertjes, and F. M. Visscher, *J. Soc. Dyers Colour.*, **81**, 400 (1965).

[13] D. C. Neckers and A. P. Schaap, *J. Org. Chem.*, **32**, 22 (1967).

[14] (a) Intermediates of the types **5** and **7**, shown in Charts III and IV, have been considered by Griffin (E. J. O'Connell, Ph.D. Thesis, Yale University, 1964, p 56, and ref 4 and 14b); (b) G. W. Griffin, E. J. O'Connell, and H. A. Hammond, *J. Amer. Chem. Soc.*, **85**, 1001 (1963).

[15] Melting points were taken on a hot stage and are corrected. Ir spectra were recorded on a Beckman IR-8; nmr on Varian A-60, A-60A, or T-60; uv on a Cary 11 or 15.

oxygen-free nitrogen[16] was bubbled through the photolysis solution.

Filter Solutions. The system used in all photolyses consisted of: cell 1, 127.0 g/l. of nickelous sulfate hexahydrate in 3.6 *N* sulfuric acid; cell 2, 137.0 g/l. of cobalt sulfate hydrate in 3.6 *N* sulfuric acid; cell 3, 29.0 g/l. of copper sulfate pentahydrate. The properties of the filter were: 290 nm, 0% T; 300, 2%; 310, 18%; 320, 36%; 327 nm (max), 41%; 330, 40%; 340, 32%; 350, 18%; 360, 5%; 370, 0%. The filter solutions were monitored before and after the photolyses to verify their stability.

Actinometry. The potassium ferrioxalate actinometer of Hatchard and Parker[17] was used, with a quantum yield of 1.23 over the wavelength range employed. The light was monitored before and after each photolysis, and corrected for light passing through the sample cell.

Liquid–Liquid Partition Chromatography. A two-phase system was prepared from 1000 ml of distilled cyclohexane, 400 ml of reagent dimethylformamide, 250 ml of ethyl acetate, and 30 ml of water. To 700 g of Eagle-Picher FW80 Celite was added 305 ml of lower phase. This was packed in a 4.1 × 150 cm thermostated column and eluted with upper phase. The optical density of the eluent was scanned at 260 nm, and 40-ml fractions were taken.

Solvents and Reagents. *trans*-Dibenzoylethylene (Aldrich) was recrystallized from ethanol, mp 110–111°. Benzophenone (Eastman Kodak White Label) was decolorized twice with Norit and recrystallized three times from ethanol. Reagent grade 2-propanol was distilled. Reagent grade benzene was distilled and stored over sodium. Reagent grade ethanol (95%) was used without further purification. Triphenylene (Aldrich) was recrystallized from benzene, mp 200–202°.

Preparation of *cis*-Dibenzoylethylene. *trans*-Dibenzoylethylene (2.32 g, 9.84 mmol) in 750 ml of 95% ethanol was irradiated for 9.0 hr at *ca.* 2.5 mEinsteins/hr using the apparatus and filters described. The solution was concentrated under vacuum to yield a white solid which was recrystallized from ethanol to yield 1.76 g (7.46 mmol, 76%) of *cis*-dibenzoylethylene, mp 135–137° (lit.[18] mp 134°).

Irradiation of *cis*-Dibenzoylethylene. *cis*-Dibenzoylethylene (648 mg, 2.64 mmol) in 750 ml of 2-propanol was irradiated 4.50 hr using the apparatus and filters described. Initial and final light intensities were 5.47 and 4.89 mEinsteins/hr with a total light absorption of 23.2 mEinsteins. Concentration under vacuum and liquid–liquid chromatography yielded in fractions 34–41, 201 mg (0.680 mmol) of 2-propyl 4-phenyl-4-phenoxy-3-butenoate; fractions 52–102, 446 mg (1.89 mmol) of *trans*-dibenzoylethylene; total material recovery, 97%; conversion, 26%; quantum yield of appearance, 0.029; of disappearance, 0.032. A total of three runs gave an average quantum yield of 0.030 ± 0.05.

Characterization of 2-Propyl 4-Phenyl-4-phenoxy-3-butenoate. The rearrangement product was an oil which was molecularly distilled at 100° (0.1 mm) to afford a colorless oil which partially solidified at room temperature. It was characterized by its synthesis[4] and the following properties: ir (neat or $CHCl_3$) 3.35, 5.78 (ester carbonyl), 5.95 (weak, phenyl enol ether), 6.25, 8.23, 8.50, 9.00, 13.30, and 14.45 μ; nmr ($CDCl_3$) τ 2.4–3.3 m (10 H, aromatic), 4.0 t (J = 7, 1 H, vinyl), 5.05 sept (J = 6, 1 H, isopropyl CH), 6.8 d (J = 7, 2 H, aliphatic), and 8.84 d (J = 6, 6 H, isopropyl methyls).

Calculation of Singlet Reaction in Triphenylene Runs. The amount of direct light absorption by the sensitizer and substrate was calculated by dividing the spectral region from 290 to 370 nm into 10-nm intervals and in each interval measuring the absorbance of the solution with and without sensitizer present. Each absorbance value was multiplied by the transmittance of the filter at that wavelength and the output of the lamp[19] at that wavelength. The results were summed over all wavelengths for each solution and the ratio of the totals was taken as the per cent light capture by the dibenzoylethylene.

The amount of singlet sensitization was calculated from the relative rates of singlet decay and energy transfer. The rate of singlet decay is[5b]

$$k_\mathrm{d} = \frac{1}{\tau} = 2.73 \times 10^7[{}^1\mathrm{T}]\ \mathrm{sec}^{-1}$$

where $[{}^1\mathrm{T}]$ is the concentration of triphenylene singlets. The rate of singlet transfer is

$$\begin{aligned} k_\mathrm{q} &= k_\mathrm{diff}[\mathrm{E}][{}^1\mathrm{T}] \\ &= 3.2 \times 10^9[\mathrm{E}][{}^1\mathrm{T}]\ \mathrm{sec}^{-1} \end{aligned}$$

as in the benzophenone calculation (see Results). The relative amount of singlet sensitization is then

$$\frac{k_\mathrm{d}}{k_\mathrm{q}} = \frac{8.5 \times 10^{-3}}{[\mathrm{E}]}$$

The amount of singlet reaction from each source was computed from the percentage of light delivered to the singlet times the quantum yield of singlet reaction.

Triphenylene Sensitization of *cis*-Dibenzoylethylene. Quantum Yield T1. *cis*-Dibenzoylethylene (94 mg, 0.39 mmol) and triphenylene (735 mg, 3.22 mmol) in 750 ml of 2-propanol was irradiated for 7.0 hr using the apparatus and filters described. The initial and final light intensities were 2.74 and 2.93 mEinsteins/hr and the total light absorption was 19.9 mEinsteins. Ultraviolet analysis showed that 17% of the light was absorbed by the *cis*-dibenzoylethylene, and the calculated per cent singlet sensitization was 11.5%. The material was chromatographed rapidly on a 3.0 × 50 cm column of deactivated silica gel slurry packed with hexane. The column was eluted with 3000 ml of hexane to give 730 mg of triphenylene and with 3000 ml of ether to give 105 mg of polar material which was subjected to liquid–liquid partition chromatography. Fractions 36–41 contained 29.7 mg (0.100 mmol) of 2-propyl 4-phenyl-4-phenoxy-3-butenoate; fractions 50–85 contained 68.6 mg (0.285 mmol) of *trans*-dibenzoylethylene; total material recovery, 98%; conversion, 25%; quantum yields (uncorrected) of appearance, 0.0050; of disappearance, 0.0053. All of the ester formed could be accounted for from the singlet.

Triphenylene Sensitization of *cis*-Dibenzoylethylene. Quantum Yield T2. *cis*-Dibenzoylethylene (43.9 mg, 0.186 mmol) and triphenylene (755.6 mg, 3.46 mmol) in 750 ml of 2-propanol was irradiated 2.00 hr using the apparatus and filters described. The initial and final light intensities were 2.70 and 2.65 mEinsteins/hr and the total light absorbed was 8.10 mEinsteins. The triphenylene was calculated to absorb 92.5% of the light and 5.5% singlet transfer occurred. The photolysis solution was concentrated under vacuum and chromatographed on a 3.0 × 50 cm column of deactivated silica gel slurry packed in 5% ether to separate the triphenylene from the reaction mixture. The mixture was subjected to liquid–liquid partition chromatography: fractions 38–47, 14.0 mg (0.047 mmol, 25%) of 2-propyl 4-phenyl-4-phenoxy-3-butenoate; 48–70, 48.7 mg, recrystallized to give 30.5 mg (0.129 mmol, 69%) of *trans*-dibenzoylethylene: total recovery, 95%; after correction for a maximum of 0.040 mmol of ester formation by singlet, quantum yield for formation, 0.001.

Triphenylene Sensitization of *cis*-Dibenzoylethylene. Quantum Yield T3. *cis*-Dibenzoylethylene (52.0 mg, 0.220 mmol) and triphenylene (3.710 g, 16.30 mmol) in 750 ml of 2:1 2-propanol–benzene was irradiated for 3.0 hr with initial and final incident light intensities of 2.53 and 2.49 mEinsteins/hr. The total light absorbed was 7.59 mEinsteins. Ultraviolet analysis indicated that the *cis*-dibenzoylethylene absorbed 2% of the light. The calculated per cent singlet sensitization was 65.%. The photolysis solution was concentrated under vacuum and chromatographed rapidly on a 4.0 × 50 cm column of silica gel slurry packed with hexane. Elution with 3000 ml of hexane afforded 3.71 g of triphenylene and 3000 ml of ether gave 60 mg of material which was subjected to liquid–liquid partition chromatography: fractions 38–49, 15.3 mg (0.0517 mmol, 23%), 2-propyl 4-phenyl-4-phenoxy-3-butenoate; 51–70, 28.5 mg (1.121 mmol, 55%), *trans*-dibenzoylethylene; total material balance, 78%; conversion, 45%; quantum yields (uncorrected) of disappearance, 0.013; appearance, 0.0068. Correction for a maximum of 2% direct absorption and 6.5% singlet transfer (quantum yield 0.03) gives a quantum yield of appearance of 0.0039. This should be a minimum value, due to lost material.

Benzophenone Sensitization of *cis*-Dibenzoylethylene. Quantum Yield B1. *cis*-Dibenzoylethylene (362 mg, 1.52 mmol) and benzophenone (10.036 g, 55 mmol) in 750 ml of 2-propanol was irradiated 3.0 hr with an incident light intensity of 3.16 mEinsteins/hr. The total light absorbed was 9.48 mEinsteins. The calculated per cent triplet transfer was 28%. The photolysis mixture was concen-

---

(16) L. Meites and T. Meites, *Anal. Chem.*, 20, 984 (1948).

(17) C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc., Ser. A*, **235**, 518 (1956).

(18) J. B. Conant and R. E. Lutz, *J. Amer. Chem. Soc.*, **45**, 1303 (1923).

(19) High brightness mercury arc lamps, Capillary Type A-H6 and B-H6, Application Data and Accessory Equipment, Outdoor Lighting Department, General Electric Co.

trated under vacuum and the benzopinacol filtered off. The benzophenone and *cis*-dibenzoylethylene were sublimed off at 45° (0.1 mm) to leave 1.55 g of material which was subjected to liquid–liquid partition chromatography. Fractions 47–55 contained 708 mg of benzophenone; 56–66, 40.5 mg of *trans*-dibenzoylethylene; 67–130, 709 mg of a mixture of dibenzoylethane and benzopinacol. The mixture was triturated with $CHCl_3$ to separate the dibenzoylethane from the benzopinacol. The dibenzoylethane was recrystallized from $CHCl_3$ to yield 35.5 mg (0.149 mmol, 10%). The quantum yield for formation was 0.016.

Identification of Dibenzoylethane. Dibenzoylethane was identified by comparing its melting point, ir, and nmr with those of known samples: mp 142–144° (lit.[20] mp 145–147°); ir[21] ($CHCl_3$) 3.45, 5.97, 6.27, 6.93, 8.25, 10.10, 15.00 μ; nmr ($CDCl_3$) τ 1.8–2.1, 2.3–2.8 m (10 H, aromatic), 4.52 s (4 H, methylenes).

Benzophenone Sensitization of *cis*-Dibenzoylethylene. Quantum Yield B2. *cis*-Dibenzoylethylene (88.5 mg, 0.375 mmol) and benzophenone (5.874 g, 32.2 mmol) in 750 ml of 2-propanol was irradiated using the apparatus and filters described for 4.00 hr (intensity 3.48 mEinsteins/hr). The total light absorbed was 13.92 mEinsteins. The calculated per cent triplet transfer was 8.7%. The photolysis solution was concentrated under vacuum and the benzopinacol filtered off. The residue was sublimed at 40–50° (0.1 mm) to remove benzophenone and dibenzoylethylene and leave 115 mg to be subjected to liquid–liquid partition chromatography: fractions 48–69, 37.7 mg, benzophenone; 70–75, 24.6 mg (0.103 mmol, 27%), dibenzoylethane; 76–102, 28 mg, benzopinacol; 103–126, 27.5 mg, dibenzoylethylene; quantum yield of appearance, 0.0074.

Benzophenone Sensitization of *cis*-Dibenzoylethylene. Quantum Yield B3. *cis*-Dibenzoylethylene (80.0 mg, 0.339 mol) and benzophenone (10.44 g, 57.3 mmol) in 750 ml of 2-propanol was irradiated 3.00 hr using the apparatus and filters described. The initial and final incident light intensities were 2.29 and 2.24 mEinsteins/hr and the total light absorbed was 6.81 mEinsteins. The calculated per cent triplet transfer was 7.9%. The photolysis mixture was concentrated under vacuum and benzopinacol (1.0363 g) was filtered off. The residue was sublimed at 45° (0.1 mm) to remove benzophenone and *cis*-dibenzoylethylene. The residue from the sublimation (1.97 g) was chromatographed on a 2.5 × 125 cm column of deactivated silica gel slurry packed in 5% ether–hexane, and washed with hexane. Fractions of 250 ml were collected. Fractions 1–7, hexane, 10 mg, unidentified; 8–11, 1% ether–hexane, nil; 12–15, 2%, 212 mg, benzophenone; 16–24, 5%, 1697 mg of benzophenone; 25–33, 5% 49 mg, mostly dibenzoylethane. Fractions 25–33 were recrystallized from ether–hexane to yield 28.1 mg (0.118 mmol, 35%) of dibenzoylethane; quantum yield of appearance, 0.017.

Benzophenone Sensitization of *cis*-Dibenzoylethylene. Quantum Yield B4. *cis*-Dibenzoylethylene (62.4 mg, 0.264 mmol) and benzophenone (6.022 g, 32.9 mmol) in 750 ml of 2-propanol was irradiated 1.00 hr using the apparatus and filters described. The initial and final light intensities were 2.24 and 2.49 mEinsteins/hr and the total light absorbed was 2.37 mEinsteins. The calculated per cent triplet transfer was 6.3%. The photolysis solution was concentrated under vacuum and the benzopinacol filtered off. The residue was sublimed at 45° (0.1 mm) to remove benzophenone and *cis*-dibenzoylethylene and leave 0.420 g of material which was chromatographed on a 2.5 × 125 cm column of deactivated silica gel slurry packed in 5% ether–hexane and washed with hexane. Fractions of 250 ml were taken: 1–8, hexane, and 9–16, 1% ether–hexane, 328 mg, benzophenone; 17–20, 1%, 21–22, 2%, 23–24, 5%, 25, 10%, and 26–28, 100%, 77.5 mg of a mixture of dibenzoylethane and benzopinacol. The mixture was rechromatographed on a 1.0 × 50 cm column of deactivated silica gel slurry packed in 1% ether–hexane and 50-ml fractions were taken; fraction 3, 1%, 41 mg, recrystallized to yield 16 mg (0.067 mmol) of dibenzoylethane (25%); quantum yield for appearance, 0.031.

Benzophenone Sensitization of *cis*-Dibenzoylethylene. Quantum Yield B5. *cis*-Dibenzoylethylene (55.9 mg, 0.227 mmol) and benzophenone (6.084 g, 33.4 mmol) in 750 ml of 2-propanol was irradiated 1.00 hr using the apparatus and filters described. The initial and final light intensities were 2.82 and 2.59 mEinsteins/hr and the total light absorbed was 2.71 mEinsteins. The calculated per cent triplet transfer was 5.7%. The photolysis solution was concentrated under vacuum and the benzopinacol was filtered off. The remainder was sublimed at 45° (0.1 mm) to remove benzophenone and *cis*-dibenzoylethylene, leaving 55 mg of material which was chromatographed on a 2.5 × 100 cm column of silica gel slurry packed with 5% ether–hexane and washed with hexane. Fractions of 250 ml were collected: 1–3, hexane, nil; 4–6, 1% ether–hexane, nil; 7–10, 2%, 2.5 mg, unidentified; 11–15, 5%, 34 mg, benzopinacol; 16–18, 5%, 12 mg (0.050 mmol, 22%), dibenzoylethane; 19–22, 5%, 5 mg, unidentified (no C=O); quantum yield for appearance, 0.019.

Acknowledgment. Support of this research by the U. S. Army Research Office (Durham) is gratefully acknowledged. Appreciation is expressed to Mr. R. Lura and Dr. T. Dooley for efforts in preliminary studies.

---

(20) P. S. Bailey and R. E. Lutz, *J. Amer. Chem. Soc.*, **70**, 2412 (1948).

(21) Catalog of Infrared Spectrograms, Samuel P. Sadtler, Philadelphia, Pa., No. 23263.