

15–20 μsec although a noticeable “tail” persists for as long as 100 μsec . The monitoring source was a PEK 75-w, mercury-xenon lamp, Type 1621, powered by storage batteries. This lamp was mounted on an optical bench in series with a collimating lens, the flash chamber, a focusing lens, and a Jarrell-Ash 500-mm Ebert spectrometer. The analyzing beam, after passing through the sample cell, was focused on the entrance slit of the spectrometer. Light intensity was measured by means of a Sylvania 931-A photomultiplier tube located at the exit slit of the spectrometer. The output from the phototube was fed into a cathode-follower amplifier and then into a Tektronix 531, wide-band oscilloscope. Oscillographs were photographed with a DuMont, Model 302, oscillograph-record camera. A Rutherford, Model A-4, time-delay generator was used to trigger the oscilloscope sweep prior to the discharge of the flash lamps and thus provided a reference for light intensity reaching the detector in the absence of triplet-triplet absorption. Circuitry for similar apparatus has been described in detail by Porter.¹¹

The cylindrical Pyrex sample cells were 21 cm in length and had a 15-mm o.d.; flat Pyrex windows were fused to the ends. Many cells were also equipped with outer jackets for filter solutions. The annulus of the filter sleeve was 6 mm. The cells were connected by side arms to bulbs where solutions were placed during the degassing procedure. The cells were cleaned with soap solutions and rinsed repeatedly with distilled water prior to use.

Solutions were degassed by attachment to a vacuum manifold equipped with a pumping system capable of evacuation to 10^{-7} – 10^{-6} mm. Dow-Corning, high-vacuum, silicone grease was used to lubricate all joints and stopcocks. Samples were frozen to the temperature of liquid nitrogen, evacuated, isolated from the system during a thawing cycle, and then refrozen, and again pumped down. The cells were sealed after five freeze-pump-thaw cycles.

Despite the inclusion of a light baffle in the chamber, stray light from the flash lamps sometimes caused problems in experiments with short-lived triplets. In this respect, it was advantageous to monitor the experimental solution at the wavelength of a principal mercury line whenever this occurred near the maximum of sensitizer triplet-triplet absorption. At these wavelengths, the emission from the monitoring source was considerably more intense, so that the signal to stray light ratio was greater. Stray light was rarely a problem in measurement of transient lifetimes greater than 100 μsec .

The oscillograph transparencies were enlarged with a slide projector and the images were traced and measured. Since the response of the photoelectric detector was linear over the range of

light intensities employed, the data for absorbance of the sensitizer triplets were analyzed by the method of Linschitz and Sarkanen.¹⁹ In practice, this operation was performed by an IBM 7090 computer which gave best values for the coefficients of first- and second-order terms.

Whenever the absorption characteristics of the sensitizers were appropriate, filter solutions were used to prevent direct excitation of the olefinic substrates by the excitation flash. Table IX gives the critical characteristics of filter solutions used.

Table IX. Filter Solutions

Solution no.	Solute ^a	Concn, <i>M</i>	Wavelength, \AA ^b
1	<i>trans</i> -Stilbene	1.4×10^{-4}	3300
2	<i>trans</i> -Stilbene	2.1×10^{-3}	3380
3	<i>trans,trans</i> -1,4-Diphenyl-1,3-butadiene	1.2×10^{-4}	3610

^a Benzene solutions. ^b Below which *A* (absorbance) > 2 for 1 cm of solution.

Because the absorbing solutes undergo photoisomerization, absorption by the filter solutions changes with time so each solution was used for only a few flashes. The light from the monitoring source was passed through a Corning 3060 glass color filter, mounted on the optical bench to prevent excitation of the quenchers during the kinetic measurements.

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Mechanisms of Photochemical Reactions in Solution. XL.¹ Steric Hindrance to Energy Transfer

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Abstract: Derivatives of benzophenone in which the two *ortho* positions of one of the aromatic rings are substituted by alkyl groups have been studied as photosensitizers for the *cis*–*trans* isomerization of the stilbenes. Compounds in which the substituents are methyl groups show behavior virtually identical with that of the parent compound. However, introduction of two isopropyl groups effects a substantial change. We infer that the bulky substituents decrease the rates of energy transfer and that transfer to the *cis* isomer is the more sensitive of the two processes to steric hindrance. In the course of the work the appearance of photoenols was observed and studied in detail in two cases. In both systems two enols, believed to be stereoisomers, were produced from a single ketone.

A mechanism of photosensitized reactions that was apparently first suggested by Franck⁴ has been shown to be applicable to photosensitized *cis*–*trans*

isomerization reactions.⁵ A key step in the mechanism is transfer of electronic excitation from an excited

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(4) J. Franck, *Z. Physik*, **9**, 259 (1922); G. Cario and J. Franck, *ibid.*, **11**, 161 (1922).

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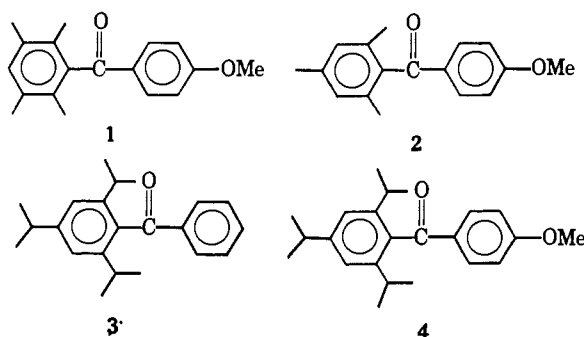
triplet state of a sensitizer to an acceptor which ultimately undergoes the observed chemical change. Efficient transfer of triplet excitation requires close contact between donor and acceptor⁶⁻⁸ so one might expect the transfer reaction to be subject to steric hindrance by suitably located bulky substituents on either donor or acceptor. If such effects are observed, they should ultimately provide useful implications concerning the preferred orientation of donor and acceptor molecules during transfer. Results of another approach to the problem have recently been reported.⁹

Results and Discussion

A series of aromatic hydrocarbons have been used to effect sensitized isomerization of the stilbenes in solution.⁵ Each sensitizer produces a characteristic photostationary state. Sensitizers having triplet excitation energies greater than ~ 60 kcal per mole give nearly identical results. Benzophenone and five closely related compounds having excitation energies lying between 65.5 and 70.1 kcal per mole all give stationary states containing $59 \pm 1\%$ *cis*-stilbene.¹⁰

Singlet-triplet absorption spectra^{11,12} indicate that vertical excitation of *cis*- and *trans*-stilbene requires 57 and 50 kcal per mole, respectively. Consequently, we infer that high energy sensitizers usually transfer energy to both isomers at the diffusion-controlled rate.^{1,5}

There is good evidence that the triplet excitation energy of benzophenone is localized largely in the carbonyl group of this molecule.¹³ With this in mind, a series of substituted benzophenones with alkyl substituents providing steric hindrance about the carbonyl group were chosen as sensitizers in an effort to test for steric effects in the process of energy transfer. Structural formulas of these ketones are shown below.



We believed that the sterically hindered sensitizers might differentiate between the stilbene isomers in the process of energy transfer and give photostationary states different from that established with benzophenone. As is summarized in Table I, the methyl-substituted benzophenones **1** and **2** and benzophenone are identical, whereas 2,4,6-triisopropylbenzophenone

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Table I. Photosensitized Isomerization of Stilbene in Benzene Solution with Sterically Hindered Benzophenones^a

	Sensitizer	E_T , kcal/mole ^b	Expected ratio ^c <i>cis</i> / <i>trans</i>	Obsd ratio <i>cis</i> / <i>trans</i>
1	2,3,5,6-Tetra-methyl-4'-methoxybenzophenone	70.2	1.47	1.45 ± 0.02
2	2,4,6-Trimethyl-4'-methoxybenzophenone	68.4	1.47	1.47 ± 0.03
3	2,4,6-Triisopropylbenzophenone	68.7	1.47	1.92 ± 0.02
4	2,4,6-Triisopropyl-4'-methoxybenzophenone	69.9	1.47	1.93 ± 0.04

^a Concentrations of substrates and sensitizers were both 0.05 *M*.

^b Triplet energy values are from ref 14. ^c This ratio was observed with solutions 0.05 *M* in both stilbene and benzophenone.

(**3**) and 2,4,6-triisopropyl-4'-methoxybenzophenone (**4**) give *cis*-rich mixtures, indicating that the transfer of energy to *cis*-stilbene is less efficient than to the *trans* isomer.

Benzophenones with alkyl substituents in an *ortho* position are known to form enols on irradiation,¹⁵ and all evidence indicates that this is a triplet state reaction. As an example, Zwicker, Grossweiner, and Yang¹⁶ studied the intramolecular photoreduction of *o*-benzylbenzophenone by flash spectroscopy. They observed two transients, believed to be the substrate triplet and the photoenol, and found that the rate of decay of the former was identical with the rate of appearance of the latter. Beckett and Porter¹⁷ investigated 2-methyl- and 2-ethylbenzophenone. On flashing, each gave unstable photoproducts identified as photoenols with absorption in the region 3400–4400 Å. The yellow color gradually disappeared over several hours and could be regenerated with an additional flash. Apparently a six-membered, cyclic transition state is essential for this tautomerization to take place, because it was not observed with 2-*t*-butylbenzophenone.

The investigation of steric hindrance to energy transfer with *ortho*-substituted benzophenones is complicated by photoenolization. It was not clear whether the results with the isopropyl-substituted benzophenones as listed in Table I should be interpreted in terms of steric hindrance to energy transfer from the ketone triplets or energy transfer from the triplet states of the corresponding photoenols. The latter would be expected to have low excitation energies and, consequently, to be selective in their action.^{1,5}

The technique of kinetic spectrophotometry was used to help resolve this problem. Compounds **2** and **4** were selected for detailed investigation. On flashing these substances in benzene solution, both formed transients with absorption maxima near 4000 Å, and the color in the solutions persisted for approximately 30 min. In addition, there was weak absorption in the same spectral region from a second set of transients

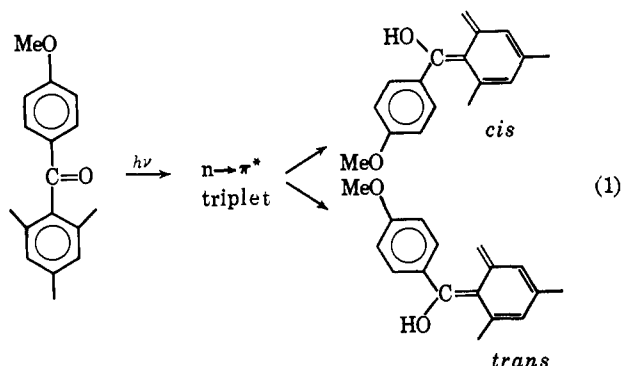
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(15) N. C. Yang and C. Rivas, *J. Am. Chem. Soc.*, **83**, 2213 (1961).

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with lifetimes close to 100 msec. The former pair of transients exhibited behavior similar to that of the photoenols observed by Beckett and Porter.¹⁷ There was no precedent for the latter pair of transients, because their lifetimes were much too long to be compatible with triplet states. However, stereoisomeric modifications of the photoenols may be produced as shown by eq 1. In the cisoid modifications, the hy-



droxyl hydrogens are more favorably situated for return to the starting position, so these species might be expected to have shorter lifetimes than the *trans* isomers. The long- and intermediate-lived transients are tentatively assigned to the transoid and cisoid modifications, respectively, of the photoenols. At longer wavelengths where the photoenols did not absorb (5460 and 5790 Å), a transient with a lifetime of approximately 50 μ sec was observed in the solution of **2**. No such transient was observed with **4**. This short-lived intermediate was believed to be a triplet, but it was uncertain whether it was the ketone or enol triplet. There was, however, no increase in enol absorption coincident with decrease in triplet absorption.

In order to check the validity of the assignment of transients to photoenols, organic bases were added to the solutions for the purpose of catalyzing the reverse tautomerization from enol to ketone. Although pyridine apparently was too weak a base, both triethylamine and 1,4-diazabicyclo[2.2.2]octane were effective in this role.

The fact that both **2** and **4** form photoenols, combined with the expectation of nearly identical triplet energies for the enols, makes it appear unlikely that enol triplets sensitized the isomerization of stilbene. If ketone triplets were responsible and if, by analogy with the results of Zwicker, Grossweiner, and Yang,¹⁶ triplet intermediates preceded enol formation, then addition of quenchers would be expected to reduce enol yields. Testing this possibility involves measuring initial absorption intensities of the photoenols following the excitation flash as a function of the concentration of suitable quenchers. Both piperylene (1,3-pentadiene) and oxygen are known to be good quenchers for triplets of compounds similar to **2** and **4**.^{4,18,19} Addition of 0.9 *M* piperylene to a solution of **4** completely quenched formation of all transients and exposure of a solution to air reduced transient formation by about two-thirds. The experiments have only semiquantitative significance since we could not ensure exact reproducibility of the amount of light absorbed by the sensitizers in different

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Table II. Quenching of Photoenol Formation by Stilbene

Sensitizer ^a (series)	Stilbene isomer	Stilbene concn, <i>M</i>	Filter soln ^b	Initial absorbance	$\Delta A/[Q]^c$
4(A)	<i>cis</i>	5.7×10^{-4}	1	3.1×10^{-1}	...
	<i>trans</i>	5.0×10^{-4}	1	2.9×10^{-1}	32
4(B)	<i>cis</i>	...	3	2.7×10^{-1}	...
	<i>trans</i>	3.0×10^{-3}	3	1.3×10^{-1}	48
4(C)	<i>cis</i>	...	2	2.1×10^{-2}	...
	<i>trans</i>	1.9×10^{-3}	2	1.1×10^{-2}	5.3
4(D)	<i>cis</i>	2.0×10^{-3}	2	9.8×10^{-3}	5.8
	<i>trans</i>	...	2	3.8×10^{-2}	...
4(E)	<i>cis</i>	1.9×10^{-3}	2	2.2×10^{-2}	8.5
	<i>trans</i>	2.0×10^{-3}	2	2.1×10^{-2}	8.5
4(F)	<i>cis</i>	...	2	3.5×10^{-2}	...
	<i>trans</i>	1.9×10^{-3}	2	2.2×10^{-2}	6.9
4(G)	<i>cis</i>	2.0×10^{-3}	2	2.1×10^{-2}	7.0
	<i>trans</i>	...	2	4.8×10^{-2}	...
4(H)	<i>cis</i>	1.9×10^{-3}	2	2.5×10^{-2}	12
	<i>trans</i>	2.0×10^{-3}	2	2.3×10^{-2}	12
4(I)	<i>cis</i>	...	2	8.0×10^{-2}	...
	<i>trans</i>	2.9×10^{-3}	2	3.5×10^{-2}	16
4(J)	<i>cis</i>	3.0×10^{-3}	2	2.7×10^{-2}	18
	<i>trans</i>	...	2	8.8×10^{-2}	...
2(K)	<i>cis</i>	2.9×10^{-3}	2	3.7×10^{-2}	18
	<i>trans</i>	3.0×10^{-3}	2	3.2×10^{-2}	18
2(L)	<i>cis</i>	...	2	8.3×10^{-2}	...
	<i>trans</i>	2.9×10^{-3}	2	3.5×10^{-2}	17
2(M)	<i>cis</i>	3.0×10^{-3}	2	3.1×10^{-2}	17
	<i>trans</i>	...	2	7.8×10^{-2}	...
2(N)	<i>cis</i>	2.9×10^{-3}	2	3.0×10^{-2}	17
	<i>trans</i>	...	3	3.1×10^{-1}	...
2(O)	<i>cis</i>	1.2×10^{-4}	3	1.0×10^{-1}	1.7×10^3
	<i>trans</i>	1.0×10^{-4}	3	1.1×10^{-1}	2.0×10^3
2(P)	<i>cis</i>	...	3	2.1×10^{-1}	...
	<i>trans</i>	1.2×10^{-4}	3	9.1×10^{-2}	1.0×10^3
2(Q)	<i>cis</i>	1.0×10^{-4}	3	9.5×10^{-2}	1.1×10^3
	<i>trans</i>	...	3	2.0×10^{-1}	...
2(R)	<i>cis</i>	1.0×10^{-4}	3	7.6×10^{-2}	1.3×10^3
	<i>trans</i>	...	3	2.0×10^{-1}	...
2(S)	<i>cis</i>	1.0×10^{-4}	3	7.5×10^{-2}	1.3×10^3
	<i>trans</i>	...	3	1.5×10^{-1}	...
2(T)	<i>cis</i>	1.1×10^{-4}	3	6.9×10^{-2}	7.7×10^2
	<i>trans</i>	1.0×10^{-4}	3	6.6×10^{-2}	9.7×10^2

^a The sensitizer concentration in all cases was 2×10^{-4} *M*.
^b Filter solution no. 1 was 2.1×10^{-3} *M* *trans*-stilbene in benzene, no. 2 was 1.2×10^{-4} *M* 1,4-diphenyl-1,3-butadiene in benzene, and no. 3 was 1.9×10^{-3} *M* carbazole in 95% ethanol. ^c In this column, [Q] represents added quencher (stilbene) concentration.

experiments. Error is introduced by variations in the optical properties of different cells as well as by fluctuations in the output intensity of the flash lamps.

Stilbene was also employed as a quencher. Filter solutions were required in order to prevent absorption of light by the stilbenes in the cells. Because the absorption spectra of the filter solutions overlap extensively with those of the hindered ketones, there was a considerable decrease in the quantity of light absorbed by the ketones. Even with high flash intensities, the yield of photoenol was small. Experimental results are summarized in Table II. For data in each series of runs in Table II, experimental conditions were kept as nearly constant as possible. The last column is the decrease in initial absorbance intensity divided by quencher concentration, and is believed to provide some measure of the efficiency with which stilbene reduced enol formation.

All solutions were monitored at 4045 Å and initial absorbance measurements include both the long- and intermediate-lived transients. Added stilbene had no

apparent effect upon the lifetimes of these transients, but only on the quantity formed. The same was true of the short-lived transient from **2** whose absorption was observed at 5460 and 5790 Å. The first-order term in the decay of this transient was $1.5 \pm 0.5 \times 10^4 \text{ sec}^{-1}$ in the presence and absence of stilbene. These results are consistent with the assignment of the short-lived transient to the triplet of one of the photoenols derived from **2**. Since the species was not quenched by either stilbene isomer up to a concentration of $3 \times 10^{-3} M$, it must have an excitation energy of less than $\sim 48 \text{ kcal/mole}$.¹

Perusal of Table II reveals that stilbene is effective in inhibiting enol formation from both **4** and **2**, although the efficiency with the former is less by a factor of approximately 50 than with the latter. Unfortunately, the poor precision of these values permits only semi-quantitative comparison of the inhibiting efficiencies of each stilbene isomer with the individual ketones. The number 50 should be corrected for the fact that the expected enolization rates of the two ketones probably differ. Walling and Gibian,²⁰ for example, have shown that in benzene solution, benzophenone triplets abstract hydrogen from cumene 3.4 times faster than from toluene. Application of this number to the differential factor in question reduces it in value to approximately 15.

Since **2** gave a stilbene photostationary state expected of a high energy photosensitizer, it seems reasonable to assume that the rates of energy transfer to the individual stilbene isomers are nearly diffusion controlled. Even if the methyl substituents do reduce the efficiency of the energy transfer process, reduction of the rates of transfer to *cis*- and *trans*-stilbene would have to be almost identical. At any rate, there is a clear indication that **4** is less reactive as an energy donor than **2** as was implied by the stationary-state measurements. Since the difference in reactivity cannot be attributed to a difference in excitation energies, we feel that the case for steric hindrance to energy transfer is strong.

Observation of a steric effect is informative. Although the excitation energy is believed to be largely concentrated in the carbonyl groups of the triplets of benzophenone and its derivatives, there has been no certainty that contact with the principal locus of excita-

tion is required to effect energy transfer. Since large groups in the vicinity of the carbonyl function can decrease reactivity, we infer that transmission of excitation to an acceptor molecule in contact with a remote part of the conjugated system is not an efficient process.

Experimental Section

Materials. Benzene (Mallinckrodt, AR) was purified by two different methods. That used in the photostationary-state determinations was treated with concentrated sulfuric acid, washed with water, and finally refluxed and distilled from sodium. The benzene used in connection with the kinetic measurements was purified by a procedure recommended by Dr. R. Steinmetz.²¹ Chloranil was dissolved in benzene to the extent of 2 g/l. The solution was contained in a well surrounding a quartz Hanovia immersion reactor with a 450-w Hanovia medium-pressure mercury lamp and was irradiated for 1 week. A brown substance that deposited on the walls of the reactor was removed daily and the supply of chloranil was replenished at the same time. The solution was passed through an alumina chromatography column to remove all colored substances and finally distilled from phosphorus pentoxide. *trans*-Stilbene (Matheson Coleman and Bell, Scintillation Grade) was recrystallized under nitrogen at Dry Ice temperatures first from methanol and then from ether. It was shown by vapor phase chromatography to contain less than 0.7% *cis*-stilbene. *cis*-Stilbene was prepared and purified by Dr. K. R. Kopecky and was shown by vapor phase chromatography to contain less than 1% *trans*-stilbene. 2,3,5,6-Tetramethyl-4'-methoxybenzophenone (**1**), 2,4,6-trimethyl-4'-methoxybenzophenone (**2**), 2,4,6-triisopropylbenzophenone (**3**), and 2,4,6-triisopropyl-4'-methoxybenzophenone (**4**) were obtained from the research stockroom of the University of Illinois²² and were used as received.

Apparatus and Procedures. All photostationary-state measurements were carried out in degassed tubes beginning with both pure *cis*- and pure *trans*-stilbene. The detailed procedure has been described previously.⁵ Analysis of the stilbene isomer distribution was made with a Loenco Model 15 gas chromatograph using a 10-ft column packed with Apiezon L (20%) on Chromosorb W. The gas chromatograph did not effect isomerization of stilbene and gave a 1:1 response to the two isomers.

The flash spectrophotometric apparatus and experimental procedure have been described elsewhere.¹

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