PHOTOISOMERIZATION OF THE STILBENES:
AN APPLICATION OF CHEMICAL SPECTROSCOPY

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ABSTRACT

Formation and quenching of stilbene triplet states by means of energy transfer is used in an attempt to elucidate the mechanism of cis-trans photoisomerization in this system.

It is found that the cis-trans ratios attained at the photostationary state in the presence of sensitizers map a "chemical spectrum" when plotted against the triplet state energies of the sensitizers. This spectrum is interpreted by assuming that stilbene triplet states can be produced by vertical or nonvertical energy transfer from the lowest triplet states of the sensitizers. A consistent picture is presented to account for the effect of sensitizer or quencher concentration on the stilbene photostationary states.

Evidence is presented which strongly supports the hypothesis that stilbene isomerization induced by direct absorption of light proceeds by way of the lowest triplet states.

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INTRODUCTION

The cis-trans isomerization of the stilbenes induced by absorption of ultraviolet light holds a unique position in photochemistry. Unlike the photoreactions which have stubbornly puzzled chemists and for which experimental results accumulate dust in patient expectation for human understanding, this reaction has long been a favorite subject for speculation. In fact, chemists have been so bold on this subject as to offer "explanations" either in advance of or despite experimental evidence. Only recently have meaningful experiments been reported which provide substance for some of these speculations.

The available evidence, chemical and spectroscopic, will be examined here and the important mechanisms will be discussed.

Quantitative measurements on photochemical reactions are in general difficult to perform. They are often complicated by factors such as the presence of quenchers or sensitizers which have been either included initially as impurities in the system or which are products of side reactions. Discovery of such factors requires constant re-evaluation of previous results and leads to experiments which take them into consideration. It is important, therefore, that much qualitative information about a photochemical reaction be available before quantitative measurements are initiated.

Since the available data on the stilbenes should be examined in the light of known, or suspected, pitfalls, these factors will be discussed first.

In addition to reversible *cis-trans* isomerization, the stilbenes undergo at least two other photoreactions. The first of these is the dimerization (1) shown in equation 1. Dimerization is observed only

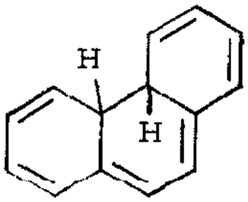
$$2\varphi CH{=}CH\varphi \xrightarrow{h\nu}$$

(1)

when very concentrated stilbene solutions are irradiated and has been reported to proceed more efficiently at higher temperatures (1, 2). It is not detected under the conditions of concentrations and temperatures usually employed for the study of *cis-trans* isomerization. The second reaction is the formation of an orange transient (3) which, in the presence of oxygen or iodine, yields phenanthrene (3, 4). Since the initial rate of formation of phenanthrene, or transient, from *cis*-stilbene is greater than its initial rate of formation from *trans*-stilbene (4b), it has been concluded that *cis*-stilbene is the precursor of the transient. In the dark, in the absence of oxygen, the transient slowly reverts to *cis*-stilbene (3). Equations 2 to 5 describe the proposed explanation for these phenomena. The transient

$$\underline{\text{cis}} \longrightarrow \underline{\text{cis}}^{**} \tag{2}$$

$$\underline{\text{cis}}^{**} \longrightarrow \text{DHP} \tag{3}$$



$$\text{DHP} + O_2 \longrightarrow \text{Phenanthrene} \qquad (4)$$

$$\text{DHP} \longrightarrow \underline{\text{cis}} \qquad (5)$$

is assumed to be dihydrophenanthrene, DHP, and may be initially formed in one of its electronically excited states. The double asterisks in equations 2 and 3 indicate singlet excitation; evidence for this detail of the mechanism will be discussed later. Equations 4 and 5 occur in the presence, as well as in the absence, of light. Since reaction 5 is slow in the dark, and since the steady-state concentration of dihydrophenanthrene during irradiation is small (see discussion), there must be efficient photochemical paths for the formation of the stilbenes from the transient in degassed solutions. The presence of dihydrophenanthrene cannot be avoided in experiments in which the stilbenes are excited by direct irradiation. Since the lowest excited singlet and triplet states of dihydrophenanthrene are probably less energetic than the corresponding stilbene states, this intermediate is a potential acceptor of either singlet or triplet state energy. In this work, it has been shown that its presence in very low concentrations ($< 10^{-3}$M) will not affect the course of the cis-trans isomerization process.

The formation of phenanthrene, equation 4, provides a very sensitive oxygen detector in the system. Oxygen is an excellent acceptor of triplet state energy and its presence could affect quantum yield measurements for the isomerization even in the absence of reaction 4. Quantum yield measurements for the isomerization should be regarded as questionable if the formation of phenanthrene was detected as a side reaction.

Finally, it has been shown that interaction between ground state stilbene molecules and excited states involved in the isomerization influences the [cis]/[trans] decay ratio of the excited states (5). This interaction is not important in dilute solutions ($\leq 10^{-3}$M) and should have little bearing on previous work.

Since in any photochemical reaction electronically excited states must of necessity be initial intermediates, it is vital to the understanding of the mechanism that as much information be obtained about these states as possible. The need for spectroscopic investigations of molecules involved in photochemical reactions cannot be overemphasized. Fortunately, this need was recognized early in studies of the cis-trans isomerization of the stilbenes, and careful spectroscopic measurements on this system were available. Since processes that convert higher electronic states to either the lowest excited singlet state or the lowest triplet state are fast (6), the latter two states are likely intermediates for photochemical reactions. Lewis, Magel and Lipkin (7) pointed out that if formation of a common excited singlet state were achieved upon irradiation of either stilbene isomer, the two isomers should have identical fluorescence spectra.

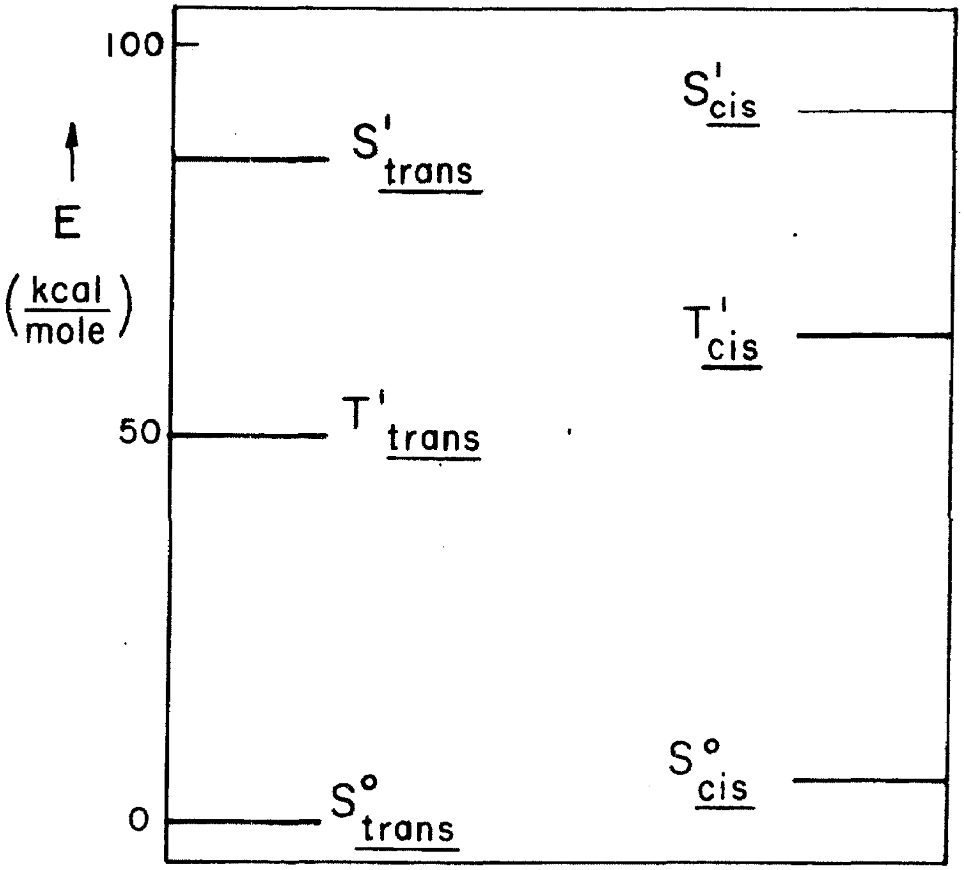
What they observed was strong fluorescence from an ether-ethanol solution of trans-stilbene at 183°K, whereas no emission could be detected from cis-stilbene under identical conditions. These observations provide a very strong argument against a mechanism involving isomerization in the manifold of electronically excited singlet states. Attempts to obtain similar information for the triplet states have up to this time been unsuccessful (8, 9c). Phosphorescence has not been observed from either isomer.

In any careful attempt to detect emission from cis-stilbene, two points must be taken into consideration. First, prolonged irradiation of cis-stilbene even at very low temperatures must be avoided since it leads to the formation of trans-stilbene and emission from the latter (7). Second, the measurements must be carried out in the absence of oxygen because otherwise phenanthrene emission is observed (9). Recently, an emission from cis-stilbene has been reported by Stegemeyer (10). This observation has been confirmed in preliminary experiments in this work and appears to be due to a species other than trans-stilbene or phenanthrene. One possible explanation is that it is fluorescence from the dihydrophenanthrene transient. This possibility will be discussed later.

Although no information could be obtained about the lowest triplet states of the stilbenes from emission studies, it was possible to obtain upper limits for their energies from their $S_0 \rightarrow T_1$ absorption spectra (11, 12). The energies of the lowest excited singlet states could be obtained accurately from the $S_0 \rightarrow S_1$ absorption spectra (12). The electronic energy levels of interest for the stilbenes are shown in Figure 1. The difference in ground state energy (~6 kcal) of the two isomers was obtained from their heats of hydrogenation (13). The higher energy content of cis-stilbene has been attributed to steric hindrance of the two ortho-hydrogens which causes the phenyl groups to twist from the plane of the central double bond.

Dyck and McClure (12) have analyzed the absorption and fluorescence spectra of trans-stilbene. They find only a slight decrease in the C=C stretching frequency (1599 cm^{-1} in S_1 vs 1635 cm^{-1} in S_0) in the lowest excited singlet state. This indicates that there is a small increase in the C=C bond length, hardly enough to greatly decrease the potential barrier for rotation about the central bond in this excited state. The absorption spectrum of cis-stilbene in a diphenylmethane matrix leads to the same conclusion. The $S_0 \rightarrow T_1$ spectrum of trans-stilbene measured either in ethyl iodide (12) or in the presence of high pressures of oxygen (11) shows very diffuse structure. As this is not the case for the $S_0 \rightarrow S_1$ absorption spectrum, here the absorption strength increases from the first to higher vibrational members. As was pointed out by Dyck and McClure, this indicates that a large Franck-Condon shift is involved. Although these authors recognized that the spectrum indicates that some basic

Fig. 1. Lowest Electronic States of the Stilbenes.



change is occurring in the region of the central bond, they nevertheless assigned the 1500 cm^{-1} separation between vibrational bands to the stretching frequency of this bond. Since this frequency is high, this tentative assignment led them to the conclusion that the central bond has not been weakened sufficiently in the lowest triplet state to allow isomerization to occur in this state. The interpretation of the vibrational structure in the absorption spectra of trans-stilbene led to conclusions which are in disagreement with predictions based on LCAO-MO calculations (14). The assignment of the central bond stretching frequency in the first excited singlet state of trans-stilbene is almost certainly correct. It is in agreement with the absence of Franck-Condon shifts in the absorption and emission spectra involving this state and with the fact that rotation about the central bond does not occur in the excited singlet state manifold. However, evidence will be presented later which suggests that the structure in the $S_0 \rightarrow T_1$ spectrum was not assigned to the proper vibrational mode.

Two types of measurements have been made on the photoisomerization of unsubstituted as well as ring substituted stilbenes. These are photostationary [cis]/[trans] ratios and quantum yields for both the cis→trans and the trans→cis directions. The influence of temperature, solvent, concentration, and wavelength of the exciting light on these quantities has been determined for some systems. The quantitative nature of these results is questionable, since there are few instances of agreement between different workers, but certain conclusions are inescapable and these will be stressed in the following discussion.

The first measurements of trans→cis quantum yields as a function of wavelength of the exciting light were attempted by Smakula (15). His work will be mentioned here merely because its results still perplex some stilbene photochemists. The experiments reported were conducted in the presence of oxygen and in some cases the formation of phenanthrene was detected. Furthermore, in the calculation of trans→cis quantum yields it was assumed that the cis→trans yield is zero. Since in some cases irradiation was carried out until as much as 90% of the trans-stilbene had been converted to cis-stilbene, any resemblance between Smakula's results and actual quantum yields is purely coincidental. As has been pointed out by Lewis et al. (7), even such resemblance is lacking.

Values of quantum yields determined by Lewis et al. (7), Hausser (16), Yamashita (17) and, to some extent, Stegemeyer (10), are not reliable. Under the experimental conditions employed by these workers, phenanthrene formation must compete with the isomerization process. Ironically, Stegemeyer, who was aware of this problem, reports quantum yields which are corrected for phenanthrene formation. His failure to prevent this complication by degassing his solutions reflects his erroneous belief that phenanthrene formation does not depend upon the concentration of oxygen in the reaction mixture (4b).

Three sets of fairly reliable measurements are available. The first involves the work of Schulte - Frohlinde and coworkers (5). Their results are mainly concerned with ring substituted stilbenes. They find that whereas different solvents do not affect the cis→trans or trans→cis quantum yields of unsubstituted stilbene or 4,4'-dinitrostilbene, substitution of one of the nitro groups in the latter compound with an electron donating group results in the dependence of the trans→cis quantum yield upon the polarity of the solvent. This effect is most pronounced when the substituents are in the 4 and 4' positions and diminishes in importance when 4 and 3' substitution is involved. Since cis→trans quantum yields are less sensitive to the solvent, the result is that for 4-nitrostilbenes, substituted with methoxy, amino, or dimethylamino groups in the 4'-position, the photostationary states depend very markedly upon the solvent used. Table 1 shows the results for 4-nitro-4'-methoxystilbene . The solvent effect is even more dramatic for the other two compounds mentioned. The best evidence that the quantum yields for stilbene isomerization are independent of wavelength of exciting light is also provided by the work on substituted stilbenes (5). The data for the isomerization of 4-nitro-4'-dimethylaminostilbene in cyclohexane as a function of exciting wavelength are shown in Table 2. The dependence of the stationary state on the exciting wavelength is as expected from the change in the

Table 1. Quantum Yields for Isomerization of 4-Nitro-4'-methoxystilbenes (exciting wavelength 3660 Å)

Solvent	% cis at Stationary State	$\varphi_{t\rightarrow c}$	$\varphi_{c\rightarrow t}$
Cyclohexane	91	0.67	0.24
Benzene	73	0.40	0.43
Paraffin oil	74	0.34	0.26
Chloroform	56	0.17	0.37
Ethanol	60	0.13	0.40
Methanol	29	0.07	0.48
Dimethylformamide	17	0.035	0.42

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Table 2. Quantum Yields for Isomerization of 4-Nitro-4'-dimethylaminostilbene in Cyclohexane

Exciting Wave-length (mμ)	% cis at Stationary State	$\varphi_{t\rightarrow c}$	$\varphi_{c\rightarrow t}$
313	19.0	0.14	0.45
366	52.5	0.20	0.40
405	60.5	0.16	0.42
436	64.0	0.16	0.37

ratios of the extinction coefficients of the two isomers with wavelength. Finally, it has been shown that whereas the quantum yield for the cis→ trans-isomerization of 4-nitro-3'-methoxystilbene increases with increasing concentration of the stilbenes, the trans→cis quantum yield decreases drastically. This effect will be discussed at some length later in connection with results from this work.

The work of Malkin and Fischer (18) is mainly concerned with the effect of temperature on the quantum yields for isomerization.

Their preliminary results for the stilbenes are shown in Table 3.

Table 3. Quantum Yields for Isomerization of the Stilbenes in Methylcyclohexane-Isohexane Solvent Mixture (exciting wavelength 3130 Å)

Temperature (°K)	% cis at Stationary State	$\varphi_{t\to c}$	$\varphi_{c\to t}$
298	94±1	0.5	0.25
243	90	0.5	0.34
183	77	0.18	0.37
153	61	0.075	0.36
133	47	0.037	0.34
113	36	0.016	0.2
93	25	0.006	0.13

The *trans*→ *cis* quantum yield becomes sensitive to the temperature of the reaction mixture below about 229°K, whereas the *cis*→ *trans* quantum yield appears to become temperature dependent only below 133°K.

That the results of Malkin and Fischer are qualitatively correct, at least for the *trans*→ *cis* quantum yields, is indicated by the work of Dyck and McClure (12), who find a similar temperature effect on the initial rates of isomerization of *trans*-stilbene and *trans*-4-bromostilbene. The latter workers have also found that a corresponding temperature dependence is shown by the relative yields of fluorescence from *trans*-stilbene. This effect is less pronounced for *trans*-4-chlorostilbene and *trans*-4-fluorostilbene, and is almost absent in the case of *trans*-4-bromostilbene.

As has been pointed out by Schulte-Frohlinde (5), the origin of a temperature effect observed by Stegemeyer (2) in the stationary states of the stilbenes in the region of 298 to 373°K is questionable because of the high stilbene concentrations involved in his experiments. His results were, almost certainly, complicated by interactions between excited and ground state stilbene molecules, and it is likely that stilbene dimerization, as well as dihydrophenanthrene formation, should make them even more difficult to interpret.

The mechanisms proposed to account for the isomerization are numerous. In some instances, these are partially based upon incorrect results. For example, Yamashita (17) was misled by the erroneous assignment of phenanthrene phosphorescence to *cis*-stilbene and Mostoslavskii (19) based his mechanism upon Smakula's report (15) that the *trans*→*cis* quantum yield for stilbene was dependent upon the wavelength of the exciting light. Such mechanisms will not be considered here.

Since the results of Schulte-Frohlinde (5) indicate that the quantum yields are independent of exciting wavelength, the lowest excited singlet states of the stilbenes are logical initial intermediates. As has been pointed out, the possibility that isomerization might occur in these states was ruled out by the spectroscopic results of Lewis *et al.* (7), and later, more conclusively, by the results of Dyck and McClure (12).

In the absence of electronic energy transfer processes there are four paths for the dissipation of energy from the lowest excited singlet states (6): chemical reaction, fluorescence, radiationless internal conversion to an excited ground state, or intersystem crossing into the triplet state manifold. Stilbene dimerization and formation of dihydrophenanthrene probably are examples of the first path but, as has been pointed out, these reactions have little bearing on the isomerization process. The second path, fluorescence, would lead to return to the ground state without isomerization. Since trans-stilbene fluoresces strongly at lower temperatures, it must, at least partially, account for the decrease in the trans→cis quantum yields. It does not appear to be an important path for the dissipation of energy from cis-stilbene at any temperature.

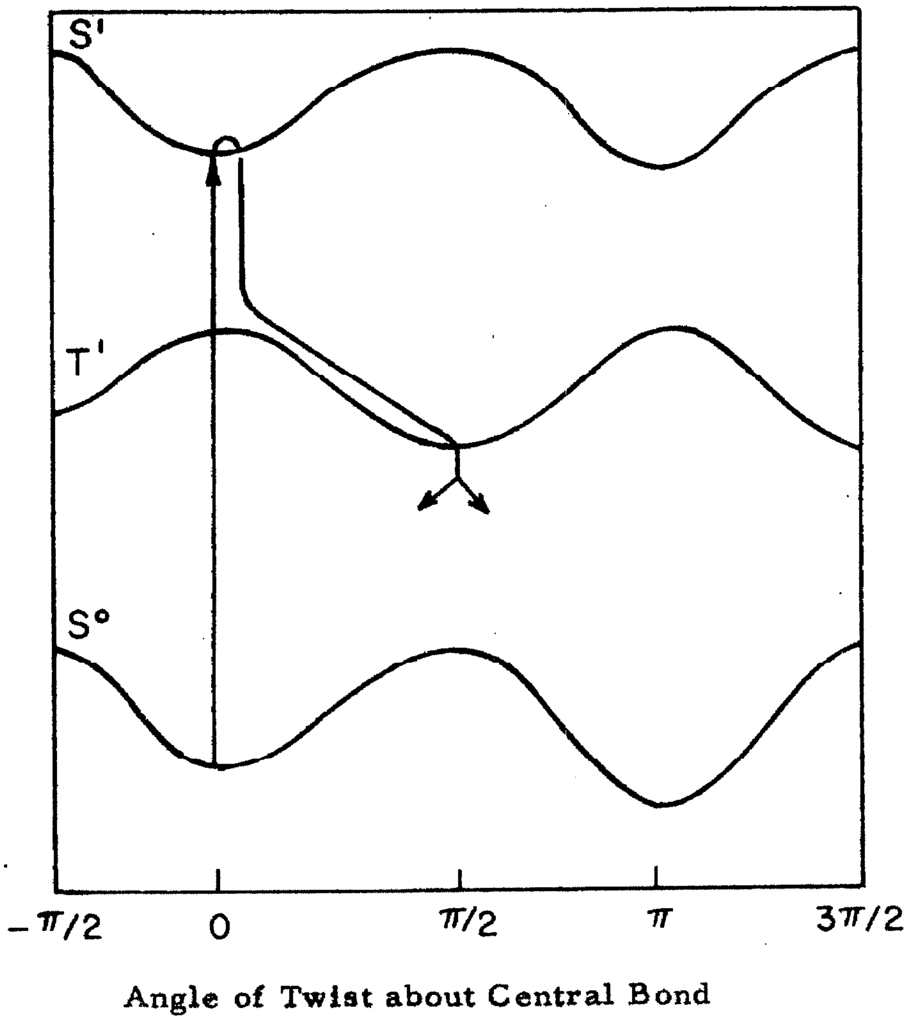
The second path for energy dissipation, internal conversion to an excited ground state, provides a possible route for isomerization. The initial ground state produced in this manner would be about 40 kcal per mole more energetic than the transition state for rotation about the double bond (20, 21). It is therefore conceivable that the molecule would pass through a condition of free rotation about the central bond before returning to either ground state. This mechanism for isomerization was proposed by Lewis, Magel and Lipkin (7) at a time when the triplet state theory had not been well developed. Actually, this mechanism is in accord with all the experimental results presented thus far. To explain the observed temperature effects within its framework, one need only postulate that internal conversion is an activated process.

By far the most popular mechanism for the isomerization has been one involving intersystem crossing to triplet states. This is an especially attractive path for stilbenes substituted with nitro or bromo groups. These groups are known to enhance intersystem crossing relative to fluorescence and internal conversion in other aromatic compounds (22) and should have a similar effect in this system. Although the intermediacy of triplet states has been presumed by several authors, there is considerable disagreement among them regarding the number of triplet intermediates.

Förster (23) was the first to propose one common intermediate triplet state. Schematically his mechanism is represented by Figure 2. Förster, however, also points out that the possibility that several triplet states are actually in equilibrium with each other cannot be excluded.

The prejudice in favor of a minimum at 90° in the potential energy curve with respect to angle of twist about the central bond probably stems from Mulliken's results for ethylene (24). Extensive calculations on this system showed that both the lowest excited singlet state and the lowest triplet state in ethylene have minimum energies when the two methylene groups in the molecule lie in planes which

Fig. 2. Förster's Mechanism for <u>cis-trans</u> Isomerization.



are perpendicular to each other. That this picture need not apply for substituted ethylenes was pointed out by Mulliken and Roothaan (24), and later by Birnbaum and Style (25). Actually, it is obvious that the ethylene calculations do not apply, at least for the potential energy curve of the lowest excited singlet states of the stilbenes. If the calculations did apply, a common singlet state intermediate would be observed, a fact which, as has been pointed out, is not in accord with the spectroscopic data on the stilbenes.

One conclusion seems to be demanded by the dependence of relative isomerization quantum yields and fluorescence quantum yields on temperature. An activated process is competing with fluorescence and this process leads to isomerization. If this process is intersystem crossing, the results of McClure with the halogen substituted stilbenes can be fairly easily rationalized. The fact that for bromine, the heaviest halogen substituent studied, the relative yield of fluorescence is practically temperature independent makes it very attractive to assume that, in this case, intersystem crossing, which was competing with fluorescence at the lower temperatures for other stilbenes, predominates at even very low temperatures. This is in accord with the expected enhancement of spin-orbital interaction by heavy atoms (22). An important consequence of the assumption that the efficiency of intersystem crossing for 4-bromostilbene is essentially temperature independent, is the necessity of finding another activated step in the mechanism for isomerization which will account for the sharp decline of the trans→cis quantum yield at temperatures below 100°K. Such a step could be the equilibration of a trans triplet with a triplet with a non-transoidal configuration. If this latter triplet were of slightly higher energy than the trans triplet and if cis-stilbene could be obtained solely by means of its decay, the observed temperature effect on the trans→cis quantum yields of trans-4-bromostilbene can be explained.

The solvent effects observed by Schülte-Frohlinde (5) on the quantum yields for isomerization can be explained either by assuming that due to its relatively long lifetime the mode of decay of the lowest excited trans singlet state could be dependent upon solvent, i.e. that polar solvents greatly enhance fluorescence relative to intersystem crossing, or by assuming that the [trans] to [cis] decay ratio from the triplet states is very solvent dependent for certain substituted stilbenes. Although only the former explanation was considered by Schülte-Frohlinde, the second is not without merit. It is possible that intersystem crossing into the triplet state manifold for nitrostilbenes may be independent of solvent (22).

At the outset of the present work, two approaches were available as routes to a more intimate understanding of the mechanism of the reaction. The first involved the possibility of detecting long-lived triplet state intermediates of the stilbenes by means of double flash spectroscopy. This approach has been unsuccessful in the past, in the case of the stilbenes (26), probably because the lifetime of the triplets involved is shorter than had been anticipated. The second approach, which was the one undertaken, was the study of the chemistry of stilbene triplets produced indirectly by means of energy transfer. Evidence that stilbene triplets could be formed indirectly by energy transfer from biacetyl had been already presented by Bäckström and Sandros (27). Triplet state energy transfer to the piperylenes had been shown to effect their isomerization (28), and an analogous study of the stilbenes was immediately undertaken. Since this work was initiated, two other groups have reported preliminary experiments on the sensitized isomerization of the stilbenes (29, 30). Their results, with slight exception, are in agreement with those presented here, but seem much more limited in scope.

EXPERIMENTAL SECTION

MATERIALS

cis-Stilbene

cis-Stilbene was obtained from Dr. K. R. Kopecky. It was shown to contain less than 1% trans-stilbene by vapor phase chromatographic analysis. It was used without further purification.

trans-Stilbene

trans-Stilbene (Matheson, Coleman, and Bell, Scintillation Grade) was purified by one of three different procedures. These procedures will be referred to as (1), (2), and (3).

(1) trans-Stilbene was recrystallized from 95% ethanol, hot stage m. p.* 124.7-125.7°.

(2) trans-Stilbene was sublimed under vacuum at about 80°, hot stage m. p. 125.9°.

(3) trans-Stilbene purified by procedures (1) and (2) in that order was zone-refined by Mr. W. G. Herkstroeter. This procedure yielded trans-stilbene which contained less than 0.1% cis-stilbene as shown by vapor phase chromatographic analysis, m. p. 124.0°.

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* All melting points are uncorrected. Unless otherwise indicated, they were determined in 1 mm capillary tubes immersed in a Hershberg melting point apparatus.

Acetophenone

Acetophenone (Matheson, Coleman, and Bell, Reagent Grade) was obtained from Dr. N. J. Turro. It had been distilled under reduced pressure. The fraction boiling at 35-36° (1-2 mm) was used.

9, 10-Anthraquinone

9, 10-Anthraquinone (Eastman Kodak, Sublimed) was recrystallized from acetic acid by Dr. C. A. Stout, m. p. in sealed tube, 285.5°.

Fluorenone

Fluorenone (Matheson, Coleman, and Bell, Reagent Grade) was purified by three procedures.

(1) It was recrystallized twice from _n_-heptane, hot stage m.p. 84.3-84.7°.

(2) The phenylhydrazone derivative was obtained in 94% yield by adding 46.6 g fluorenone to 30 g phenylhydrazine and heating the reaction mixture on the steam bath for 4 hours. The phenylhydrazone was dissolved in a minimum amount of benzene and enough alumina (Merck, Neutral) was added to the solution to produce a slurry. The slurry was added to a column packed with 1500 g alumina in _n_-pentane. Elution was carried out with 2 liters _n_-pentane, 1 liter 5% diethyl ether in _n_-pentane, 1 liter 10% ether in pentane, 625 ml 20% ether in pentane, 700 ml 30% ether in pentane, and finally, 2 liters of diethyl ether.

Only the last fraction was yellow; the first six were colorless and were discarded. The chromatographed phenylhydrazone was recrystallized twice from a mixture of ethanol and water. The first crop from the second recrystallization was 40 g of yellow needles, hot stage m. p. 153.3-153.7°.

To regenerate the fluorenone from its phenylhydrazone, the procedure of McGuckin and Kendall (31) was essentially used. The pure phenylhydrazone (40 g) was added to a solution containing 620 ml glacial acetic acid, 89 ml pyruvic acid (Matheson, Coleman, and Bell, 99+% pure) and 193 ml distilled water. The resulting inhomogeneous solution was kept at 60°C under nitrogen for 24 hours. At the end of this period a homogeneous orange solution was obtained. This solution was added to 3 liters of distilled water and the resulting precipitate was filtered. The crude fluorenone was dissolved in methylene chloride and the solution was extracted with aqueous sodium bicarbonate until no more evolution of carbon monoxide was observed. After drying over calcium chloride, the methylene chloride was removed by distillation. The fluorenone crystals obtained were recrystallized first from n-heptane and again from ligroin (85-100° b. p. range), hot stage m. p. 84.8-85.0°. This fluorenone was then sublimed at 80° (about 1 mm), hot stage m. p. 84.3-84.5°.

(3) Five grams of fluorenone obtained by procedure (2) was zone refined in a sealed tube which contained a partial pressure of

nitrogen, m. p. 83.8-84.0°. Mr. W. Herkstroeter carried out this purification.

2-Acetonaphthone

2-Acetonaphthone (Eastman Kodak, White Label) was recrystallized from ligroin (60-70° b. p. range), hot stage m. p. 54.1-54.6°.

Benzil

Benzil (Matheson, Coleman, and Bell, Reagent Grade) was recrystallized from ligroin (85-100° b. p. range) , hot stage m. p. 96.2-96.6°.

3-Acetylpyrene

3-Acetylpyrene was obtained crude from Mr. H. P. Waits, m. p. 85-87°. The crude yellow compound (4.4 g) was chromatographed on 100 g alumina. Elution with n-pentane, 10% ether in pentane, and 20% ether in pentane, yielded traces of white and yellow residues and were discarded. The 3-acetylpyrene was isolated after elution with 350 ml 30% ether in pentane and 500 ml 50% ether in pentane. It consisted of pale yellow crystals, hot stage m. p. 88-90°. These crystals were dissolved in ether. To the ether solution was added carbon black and the solution was brought to boiling for a few minutes on a steam bath. It was then filtered through celite and the ether was removed by boiling. The residue was recrystallized twice from n-heptane. Pale yellow platelets were obtained, hot stage m. p. 90.4-91.0°. These crystals were short path distilled at 115° (< 1 mm). The final product was 2.9 g white needles, hot stage m. p. 89.9-90.1°.

Benzanthrone

Benzanthrone (Cal Biochem , Practical Grade) was dissolved in benzene and chromatographed on alumina. It was eluted with benzene. A black band was retained by the column. The chromatographed benzanthrone was recrystallized from methanol. The pale yellow needles melted sharply on the hot stage at 174.9°.

Duroquinone

Duroquinone (Cal Biochem , Reagent Grade), m. p. 112.7-113.7°, was used without further purification.

1,4-Benzoquinone

1,4-Benzoquinone (Matheson, Coleman, and Bell, Practical Grade) was dissolved in benzene and chromatographed on rosite. It was then recrystallized from benzene and finally sublimed, hot stage m. p. 114.5-114.7°.

1,4-Naphthoquinone

1,4-Naphthoquinone (Eastman Kodak, Practical Grade) was dissolved in benzene and chromatographed on rosite (a homogeneous mixture of carbon black (about 30%) and celite). Evaporation of the solvent resulted in yellow crystals, hot stage m. p. 125.2-126.2°, These crystals were sublimed at about 80° and 1 mm pressure before use.

Chloranil

Chloranil (Matheson, Coleman, and Bell, Reagent Grade) was used without further purification.

9-Anthraldehyde

9-Anthraldehyde (Aldrich, Research Grade) had been recrystallized twice from acetic acid by Dr. N. J. Turro. It was dissolved in a mixture of diethyl ether and *n*-pentane and treated with carbon black. After two filtrations, the solution was cooled. Yellow needles crystallized out, hot stage m. p. 105.8-106.7°.

Benzophenone

Benzophenone (Matheson, Coleman, and Bell, Reagent Grade) was recrystallized from ligroin (60-70° b.p. range), hot stage m. p. 48.5-49.1°. In the last part of this work, benzophenone was obtained from Mr. A. A. Lamola. It had been recrystallized from diethyl ether.

1-Naphthaldehyde

1-Naphthaldehyde (Eastman Kodak, White Label) was distilled at about 1 mm pressure. The fraction boiling at 97-98° was collected. The compound was slightly yellow and was redistilled. The fraction collected boiled at 103-104°C (about 1 mm). It was a colorless liquid and was stored in an amber bottle. It was refrigerated until used.

2,3-Pentanedione

2,3-Pentanedione (Eastman Kodak, White Label) was distilled by Dr. N. J. Turro, b. p. 106°, at atmospheric pressure. It was redistilled at water aspirator pressure through a stainless steel wire gauge packed column. The fraction boiling at 33° was collected for use.

Phenanthrenequinone

Phenanthrenequinone (Eastman Kodak, White Label) was dissolved in benzene and boiled in the presence of carbon black. The solution was filtered and cooled. The crystals obtained were recrystallized from acetone, hot stage m. p. 206.5-207.0°.

Phorone

Phorone (Eastman Kodak, Practical Grade) was fractionally distilled on a 2-foot column packed with glass helices. The fraction boiling at 98.5° (26 mm) was retained for use. It was a light yellow liquid, m. p. 27.5°.

Mesityl Oxide

Mesityl oxide (Eastman Kodak, White Label) was distilled by Dr. N. J. Turro. The fraction boiling at 127.5-129° at atmospheric pressure was used without further purification.

Biacetyl

Biacetyl (Matheson, Coleman, and Bell, Reagent Grade) was distilled by Dr. N. J. Turro. The fraction boiling at 89-90° at atmospheric pressure was used without further purification.

2-Naphthyl Phenyl Ketone

2-Naphthyl phenyl ketone (K and K, Practical Grade) (4 g) was dissolved in benzene (10 ml). The brown solution was chromatographed on alumina (50 g). Elution was carried out first with 70 ml n-pentane and then with benzene. The n-pentane eluent was discarded. The yellow benzene solution was passed through a column packed with 15 g rosite. The eluent was concentrated and cooled. The ketone crystallized out in white crystals, hot stage m. p. 83.5-84.3°.

Xanthone

Xanthone (Aldrich, Research Grade) was chromatographed on a combination rosite and alumina column. It was eluted with benzene. After concentration and cooling of the eluent, white crystals were obtained, hot stage m. p. 171.9-172.2°.

1-Naphthyl Phenyl Ketone

A stock solution containing 1-naphthyl phenyl ketone in benzene was obtained from Dr. N. J. Turro. The solution was concentrated and cooled. White crystals of the ketone were obtained, hot stage m. p. 76.4-77.0°. The ketone was used without further purification.

Michler's Ketone

Michler's ketone (4,4'-bisdimethylaminobenzophenone, Eastman Kodak, Practical Grade) was recrystallized twice from methanol and washed with ligroin (30-60° b. p. range) by Dr. N. J. Turro, m. p. 171.0-171.5°. It was used without further purification.

Flavone

Flavone (Aldrich, Research Grade) was used without further purification, m. p. 97.0°.

2-Naphthaldehyde

2-Naphthaldehyde (K and K, Reagent Grade) was used without further purification, hot stage m. p. 59.3-61.0°.

Azulene

Azulene (Aldrich, Research Grade) was sublimed twice by Mr. A. A. Lamola, m. p. 99.5-99.9°. It was used without further purification.

9,10-Dibromoanthracene

9,10-Dibromoanthracene was prepared by Dr. K. R. Kopecky. For the stilbene experiments it was used as found, m. p. 217.0-218.5°. It was subsequently recrystallized three times from carbon tetrachloride by Mr. F. G. Moses, m. p. 219.2-219.8°. The recrystallized material was used in the 2,3-diphenylbutene-2 experiments.

Eosin

Eosin (Student Preparation) was recrystallized from ethanol by Dr. C. A. Stout. It was used without further purification.

2-Acetylfluorene

2-Acetylfluorene (Aldrich, Research Grade) was chromatographed on alumina with benzene as the eluent. It was then recrystallized from methanol, m. p. 132.0-133.0°C. This purification was carried out by Mr. A. A. Lamola.

1,2-Benzanthracene

1,2-Benzanthracene (Eastman Kodak, White Label) was dissolved in benzene and chromatographed on rosite. The yellow color of the compound persisted through this chromatography. The benzene was evaporated and the residue was recrystallized from ethanol. The yellow crystals obtained were dissolved in benzene and chromatographed on alumina. Elution was carried out with benzene. On concentration and cooling, white crystals were obtained from the eluent, m. p. 158.9-159.0°.

Pyrene

Pyrene (Matheson, Coleman, and Bell, Practical Grade) was dissolved in benzene and chromatographed on rosite. The eluent was concentrated to dryness and the residue was recrystallized from ethanol. White crystals were obtained, m. p. 149.0-149.2°.

Acridine

Acridine (Eastman Kodak, Practical Grade) was dissolved in diethyl ether and chromatographed on rosite. The ether eluent was concentrated and ligroin (30-60° b. p. range) was added to the resulting solution. On cooling this mixture, yellow needle-like crystals were obtained, m. p. 110.0°.

4-Acetylbiphenyl

4-Acetylbiphenyl (Aldrich, Research Grade) was purified by Mr. A. A. Lamola. The purification consisted of chromatography on alumina with benzene as the eluent, treatment with carbon black in methanol, and recrystallization from methanol.

Thioxanthone

Thioxanthone (Aldrich, Research Grade) was purified by Mr. A. A. Lamola using the procedure described for 4-acetylbiphenyl, m. p. 209.0°.

Santonin

Santonin was obtained pure from Mr. M. Fisch and was used without further purification.

4-Methyl-4-dichloromethylcyclohexadienone

4-Methyl-4-dichloromethylcyclohexadienone was obtained pure from Dr. P. P. Gaspar and was used without further purification.

β-Naphthil

β-Naphthoin was prepared by the method of Gomberg and Bachmann (32). A mixture containing benzene (87 ml), diethyl ether (87 ml), iodine (14.9 g), and magnesium (10.5 g) was stirred until the iodine color disappeared. β-Naphthoic acid (Matheson, Coleman, and Bell) (15 g) was then added a few grams at a time. When evolution of hydrogen ceased, the mixture was heated to about 70° for 8 hours. The excess magnesium was removed by filtration, and to the filtrate was added benzene (50 ml) and water (200 ml). Enough hydrochloric acid was then added to dissolve the magnesium hydroxide. The organic layer was washed with several portions of sodium bicarbonate solution. The organic solvents were then evaporated to dryness at aspirator pressure. The crude β-naphthoin thus obtained was oxidized without further purification.

The oxidation was as described by Clarke and Dreger (33). A mixture was prepared containing cupric sulfate (24.6 g), pyridine (24 g), water (9.6 g), and the crude β-naphthoin. It was stirred for two hours at 80°. At the end of this period benzene was added to the mixture. The organic layer was extracted first with water and second with dilute hydrochloric acid. The benzene was removed by boiling and the residue was chromatographed on alumina. The yellow product was obtained upon elution with 20% diethyl ether in n-pentane. It was recrystallized twice from n-heptane, hot stage m. p. 160.8-

161.8°. This β-naphthil was used in some experiments and will be referred to as grade 1. It was further purified by a second chromatography on alumina, this time with benzene as the eluent, and was recrystallized from benzene, hot stage m. p. 160.1-160.8° (grade 2).

α-Naphthil

The naphthoin condensation was carried out with 1-naphthaldehyde using the procedure of Gromberg and Van Natta (34). 1-Naphthaldehyde (11 g), potassium cyanide (3.5 g), ethanol (25 ml), and water (13 ml) were mixed and kept at 78° for 11 hours. The mixture was then diluted with water (50 ml) and extracted with benzene. The benzene was removed by boiling on the steam bath and an oily residue remained. This residue was oxidized as described in the synthesis of β-naphthil (33). Work-up and chromatography on alumina yielded some yellow crystals. These were recrystallized from aqueous ethanol, then treated with carbon black and again crystallized from ethanol. The crystals were dissolved in benzene and chromatographed on alumina with benzene as the eluent. The α-naphthil thus obtained (.2 g) was finally recrystallized from ethanol, hot stage m. p. 193.0-194.0°.

Chelates

Ferric dipivaloylmethide, chromium dipivaloylmethide, and ferric dibenzoylmethide were obtained pure from Dr. R. P. Foss.

The origin and physical properties of these chelates have been reported (35).

trans-2,3-Diphenylbutene-2

Acetophenone (35 g) and hydrazine hydrate (Matheson, Coleman, and Bell, 99-100%) (22 ml) were dissolved in ethanol (75 ml). The solution was kept at 60° for one hour and was then heated to reflux for two hours. The ethanol was removed on the steam bath by means of a rotary evaporator which was connected to a water aspirator. The pale yellow oily residue (40 ml) was washed with n-pentane (300 ml). The crude acetophenone hydrazone was precipitated by cooling the n-pentane mixture in a dry ice bath. A portion of the hydrazone (5.1 g) was mixed with yellow mercuric oxide (Baker, Analytical Reagent) (16.8 g) and anhydrous sodium sulfate (Baker, Analytical Reagent) (4.4 g). To the mixture was added 100 ml ligroin (30-60° b. p. range). The mixture was stirred with a magnetic stirrer for about 15 minutes. The inorganic salts were separated by filtration. The filtrate was a ruby-red solution.

The method of Vargha and Kovacs (36) was used to convert the phenylmethyldiazomethane to the desired olefin. The ruby-red solution was cooled to 0° in an ice-water bath. Sulfur dioxide was bubbled into the cold solution until the red color disappeared. A white precipitate, probably the episulfone of trans-2,3-diphenylbutene-2, precipitated. The precipitate was separated from the yellow solution and slowly warmed to 100° . It was kept at this temperature for 90 minutes. The yellow residue obtained was chromatographed on alumina. Elution was carried out with ligroin (30-60° b. p. range). Upon concentration and cooling of the eluent trans-1,2-diphenylbutene-2 crystallized in white plates (0.4 g), m. p. 103.5-104.0°. A yellow band, probably acetophenone azine, was retained by the column. Work-up of the yellow solution obtained from reaction of sulfur dioxide with methylphenyldiazomethane yielded white crystals (0.4 g) which were shown to be a mixture of cis- and trans-2,3-diphenylbutene-2 (36% cis) by vapor phase chromatographic analysis (details of analysis will be given in connection with photostationary state composition determinations). Only the pure trans isomer was used in further experiments.

Other methods used to decompose phenylmethyldiazomethane were: (1) addition of trace iodine to an ether solution of the diazomethane, (2) thermally by refluxing in benzene, (3) photochemically by irradiation of the diazomethane through quartz (Hanovia, 450-watt medium pressure mercury lamp), and (4) addition of cuprous chloride to a solution of the diazomethane in benzene. All these methods led to evolution of nitrogen and disappearance of the red color of the solution. Analysis of the resulting yellow solutions using vapor phase chromatography on an Apiezon-L column (described later in connection with analysis of the stilbenes) showed that in each case the major product obtained was the azine of acetophenone (over 99% by area in V. P. C. traces).

Benzene

(1) Benzene (Mallinckrodt, Analytical Reagent Grade) was washed with portions of concentrated sulfuric acid until no further darkening of the sulfuric acid layer was observed. It was then washed with water and finally with a saturated aqueous sodium chloride solution. The benzene was distilled and only a middle fraction (about 75% of total volume) was retained for use. When no darkening of the sulfuric acid was observed on the first wash, the benzene was occasionally used without purification.

(2) Benzene (Phillips, Research Grade) was used without further purification. It was specified to be 99.89% pure with toluene being the most likely impurity. However, no toluene could be found by vapor phase chromatographic analysis under conditions where even a thousandth of a per cent should be detectable.

n-Heptane

n-Heptane (Phillips, Reagent Grade) was shown not to decolorize concentrated sulfuric acid. It was distilled with a 4 ft. spinning band column before use.

Methanol

Methanol (Baker and Adamson, Reagent Grade) was used without further purification.

Ethyl Iodide

Ethyl iodide (Mallinckrodt, Analytical Reagent Grade) was chromatographed on alumina and distilled immediately before use, b. p. 71.0°. This purification was carried out by Mr. W. Hardham.

Potassium Ferrioxalate

Potassium ferrioxalate was prepared using the procedure of Hatchard and Parker (37). One volume (150 ml) of a 1.5 F solution of ferric chloride hexahydrate (Baker and Adamson, Reagent Grade, Min. Assay 99.5%) in water was added to three volumes (450 ml) of a 1.5 F aqueous solution of potassium oxalate monohydrate (Baker and Adamson, Reagent Grade, Min. Assay 99.0%). The flask containing the solution was wrapped in aluminum foil and refrigerated. Green crystals of potassium ferrioxalate formed. These were recrystallized three times from warm water. The reaction to form the potassium ferrioxalate as well as the recrystallizations were carried out in a room which was dark except for the red light from an infrared lamp.

Other Chemicals

Other chemicals used in connection with the potassium ferrioxalate actinometry were reagent grade and were used without further purification.

DETERMINATION OF PHOTOSTATIONARY STATE COMPOSITIONS IN THE PRESENCE OF SENSITIZERS

Several procedures were used for the determination of the [cis]/[trans] ratios of the stilbenes attained at the photostationary state in the presence of sensitizers. These procedures differ mainly in the method of analysis.

Usually, solutions containing two different initial compositions of the stilbenes were prepared with each sensitizer. For high energy sensitizers, the initial compositions were 0 and 100% cis-stilbene. For low energy sensitizers, energy transfer was less efficient and longer times of irradiation were required. Under such conditions, side reactions involving either the sensitizer only, or the addition of the sensitizer to the stilbenes, often became important. Since the products of such reactions were often new sensitizers or interfered with the analysis, it was necessary to reduce the time of irradiation in such cases to a minimum. This was effected by irradiation of solutions in which the initial stilbene composition bracketed the expected stationary state but deviated from it slightly. The success of this method was not always overwhelming. On a few occasions, the photostationary state was approached only from one direction.

In all cases 3 ml samples of the solutions containing the desired concentration of the stilbenes and sensitizer(s) in a chosen solvent were added to each of several pyrex culture tubes (13 x 100 mm) which had been washed and dried and had been constricted about 20 mm from the top. The samples were then degassed with four freeze-degas (about 1 micron pressure)-thaw cycles. After degassing, the tubes were sealed at the constriction.

Irradiation was carried out in an apparatus known as "the merry-go-round." It was designed by Mr. F. G. Moses. As many as 24 sample tubes could be irradiated simultaneously. The tubes were held equidistant from the light source. They fitted snugly into either an inner ring of 18 circular openings, or into an outer ring of 24 openings on a rotating turntable. The tubes and the apparatus were immersed in a thermostated water bath. At the center of the rotating turntable was the inner jacket of a quartz Hanovia immersion reactor. The jacket housed a 450-watt Hanovia high pressure mercury lamp. Cold water or filter solution was circulated through the jacket during the period of irradiation. Four different filter systems were used to insure that most, or all, of the light incident upon the tubes would be absorbed by the sensitizers rather than by the stilbenes. The filter systems will be described in detail below. Samples were removed periodically from the apparatus and the [cis]/[trans] ratio of the stilbenes was determined.

To facilitate later reference, the filter systems will be numbered. (1) The first system was merely a cylindrical pyrex glass filter. Its absorption spectrum was measured with a Cary 14 spectrophotometer. It was opaque below 2900 Å and transmitted 47, 75, and 90% of the 3130, 3340, and 3660 Å mercury lines, respectively, as well as the mercury lines of longer wavelengths. Since the $S_0 \rightarrow S_1$ stilbene absorption tails extend up to 3400 Å , they absorbed some of the incident light directly. Use of this filter system was avoided when possible. (2) The second system consisted of the glass filter described above in addition to a cupric tetrammine sulfate filter solution. The solution was prepared by dissolving cupric sulfate pentahydrate (40 g) in concentrated ammonia (68 ml) and diluting to one liter with water. It was circulated through the immersion jacket (optical path, about 0.7 cm) by means of a water pump and was passed through a copper coil immersed in an ice-water bath. The ice content of the bath had to be continuously replenished since it was found that whereas the solution was stable when irradiated cold, it deposited a black precipitate on warming during irradiation. This filter system was particularly suitable for yellow sensitizers, since it transmitted only the 4045 and 4358 Å lines of mercury. (3) The third system was identical with system (2), except that the filter solution used was 0.50-0.75 F in cupric nitrate hexahydrate. The only important mercury lines transmitted by this solution were the 3660 Å line as well as lines of longer wavelengths. (4) The fourth filter system was a cylindrical uranium glass tube. This transmitted light of wavelengths longer than 3300 Å. It was essentially identical with filter system (3) in absorption properties but was much more convenient to use.

Four methods of analysis were employed for the determination of [cis]/[trans] ratios. They will be described in historical order.

(1) The first method used was ultraviolet spectrophotometric analysis of the mixtures of sensitizer and the stilbenes. This method required careful determination of extinction coefficients for each sensitizer (see following section) and was very time-consuming. Since the irradiated solutions were usually 0.050 M in stilbene and sensitizers, λ -pipets were used for dilution purposes. Optical densities were measured for methanol solutions using one cm matched quartz cells and a Beckman DU or a Cary 14 spectrophotometer. The blank solutions were methanol plus the appropriate amount of solvent present in the solutions containing the stilbenes. Inclusion of the solvent in the blank was especially critical when irradiation was carried out in benzene. The wavelengths selected for analyses were 263, 276, and 295 mμ. The 263 mμ wavelength is an isosbestic point for the stilbenes in methanol and the optical density here could be used to monitor the total stilbene concentration. Initially, the optical density was also measured at 247 mμ. Since phenanthrene absorbs very strongly at this point, it was possible to detect its formation in small amounts. Since it was shown that the formation of phenanthrene does not occur in the absence of oxygen, measurements at this

wavelength were discontinued. When other side reactions occurred, this method of analysis could not be used satisfactorily.

(2) To avoid the need for the determination of extinction coefficients for each sensitizer, the stilbenes were separated from the sensitizer by chromatography on alumina. Small columns (10 in x 0.5 in) were dry-packed with about 10 g alumina. The contents of each tube were poured on the column and eluted with benzene (8-15 ml). After concentration on the steam bath, the stilbene composition was determined by ultraviolet spectrophotometric analysis. That the chromatography did not affect the stilbene composition was demonstrated by showing that with fluorenone as the sensitizer, the same results were obtained using either of the above procedures.

(3) The most reliable method of analysis was used only in the final stages of this work. It involved vapor phase chromatography on 4-7 ft. by 1/4 in. columns packed with 20% Apiezon L on either C-22 Firebrick (42-60 mesh) or on 20 M Chromosorb P (45-60 mesh). Loenco vapor phase chromagraphers Model 15B equipped with either a thermal conductivity, or a flame ionization detector, were used. Analysis of stilbene mixtures of known composition showed that the ratio of the areas of the peaks corresponding to cis- and trans-stilbene were equal to the ratio of their concentration with either detector. Areas were automatically recorded by the disc integrators on the recorders used for analysis.

(4) In a few cases, it was found that the sensitizer interfered with the vapor phase chromatographic analysis of the stilbenes. It was therefore necessary to separate the sensitizer by chromatography on alumina, as described under procedure (2), prior to analysis by vapor phase chromatography. When the total stilbene concentration was small, it was necessary to evaporate some of the benzene before analysis. This was accomplished by warming the solutions on the steam bath under a stream of purified air. It was found that when evaporation of the solvent was allowed to go to dryness, the mixtures analyzed higher in trans-stilbene. Such results were discarded and care was taken to avoid this complication.

DETERMINATION OF PHOTOSTATIONARY STATE COMPOSITIONS FOR THE ISOMERIZATION OF THE STILBENES INDUCED BY DIRECT ABSORPTION OF LIGHT

The apparatus described by Moore (37) was used for these experiments. It consisted of a Westinghouse (SAH 800-C) 800-watt short arc, medium pressure, mercury lamp whose light was collected and collimated by mirrors so that a parallel beam of light would pass through a filter holder and cell holder mounted on an optical bench. Four 15 mm tubes placed in a Beckman D. U. ultraviolet spectrophotometer cell holder could fit into the beam.

In the first set of experiments an interference filter was used to isolate the 3130 Å mercury line. Unfortunately, this filter system had a very broad band pass (3300-2800 Å) and although its maximum transmittance was at 3130 Å, the lamp output at 3030 and 3250 Å was high, and the light incident on the solutions was not monochromatic. This is shown more quantitatively in Table 4.

Table 4. Properties of 800-Watt Lamp and 3130 Interference Filter

Wavelength (Å)	Lamp Output Watts/100 mu	Filter Transmittance (%)
3030	12.5	17.8
3130	11.7	28.4
3250	10.7	18.2

The cells used were 15 mm quartz test tubes sealed (graded seal) to a 12/30 ground-glass joint. They were constricted a short distance below the joint. The degassing and sealing procedure was as described in the previous section, except that the tubes were connected to the vacuum system by means of glass joints rather than rubber stoppers.

The stationary states were approached from both isomers and analyses for the [cis]/[trans] ratio, as well as for the properties of the orange transient formed upon irradiation,were carried out spectrophotometrically.

Four tubes, two containing trans-stilbene (0.05 M, 0.001 M) and two containing cis-stilbene (0.05 M, 0.001 M) in benzene, were irradiated simultaneously. It was noticed that build-up of yellow-orange color upon irradiation was practically instantaneous for the solutions whose initial stilbene composition was 100% cis isomer, but that the build-up of colored species in the trans-stilbene solution was very gradual.

Irradiation of the solutions was continued for a period of time sufficiently long to assure the establishment of photostationary states. About 15 minutes after irradiation was interrupted, the absorption spectrum of the transient was recorded on a Cary Model 14 spectrophotometer for the solution which was initially 0.05 M in trans-stilbene. The spectrum showed a well defined maximum at

4550 Å. The rate of disappearance of the transient was determined by measuring the decrease of optical density at 4200 Å as a function of time (Table 5 and Figure 3).

Table 5. Absorption of Transient at 4200 Å (benzene--about 30°C)

Time (t) (min)	Optical Density D	$\ln(D_{10}/D_t)$
10	0.550	0.000
15	0.530	0.039
25	0.508	0.077
30	0.497	0.104
45	0.462	0.174
70	0.399	0.322
135	0.267	0.723
195	0.172	1.163
265	0.105	1.656

When all color had disappeared from the irradiated solutions, the tubes were opened and the stilbene compositions were determined using a Beckman DU spectrophotometer.

A second series of experiments was carried out in which azulene or ferric dibenzoylmethide was included in the reaction mixtures.

These experiments were performed on the optical bench apparatus just described. A filter train consisting of a Corning C. S. 7-54 filter (3 mm), and aqueous filter solutions of nickel chloride (0.455 M, 2.5 cm path length), potassium dichromate (0.005 M, 2.0 cm path length), and potassium biphthalate (0.0049 M, 2.0 cm path length) in quartz cells, was used. The potassium biphthalate solution was renewed every 24 hours of irradiation. The only effective radiation incident upon the solutions was the 3130 Å mercury line. (Actually, 93% of the incident light was the 3130 Å line and 7% the 3340 Å line (38); however, the extinction coefficients of the stilbenes are much greater at 3130 Å and the 3340 Å radiation can be neglected.) The cells in which reaction mixtures were irradiated were 15 x 125 mm pyrex test tubes sealed to 12/30 ground glass female joints. The degassing and sealing procedure was as described previously.

Analyses for the [cis]/[trans] ratio of irradiated samples were carried out after sufficient time had elapsed to allow the colored transient(s) to disappear. The analysis used was method 3 (see experimental on sensitized isomerizations).

Immediately after irradiation and before analysis for the stilbene composition was carried out, the decrease of absorption at 4500 Å was measured as a function of time for the runs described in the fifth and seventh rows of Table 20. These measurements were initiated 2 minutes after irradiation was interrupted. A Cary 14 spectrophotometer was used. The data are shown in Table 6.

Table 6. Effect of Azulene on Formation and Disappearance of Transient(s).

Time (t) (min)	Sample 5[a] D (4500 Å)[b]	Sample 7[a] D (4500 Å)[b]
0	0.090[c]	0.075[c]
2		0.073
4	0.087	
5		0.067
9	0.080	
13	0.075	
16		0.025
21		0.015
22	0.039	
23	0.030	

a. The number refers to entry in Table 20.
b. Optical densities are corrected for the absorption of the samples before irradiation.
c. This value was obtained by extrapolation.

Extinction Coefficients of the Stilbenes and Quenchers in Benzene

The extinction coefficients of the stilbenes in the 3130 Å region, as well as the extinction coefficients of azulene and ferric dibenzoylmethide at 3130 Å in benzene, were measured using the Cary 14 spectrophotometer. They are shown in Table 7.

Table 7. Extinction Coefficients of the Stilbenes and Quenchers in the 3130 Å Region (Benzene).

	Extinction Coefficients $\times 10^{-4}$						
Wavelength (Å)	3115	3120	3125	3130	3135	3140	3150
trans-Stilbene	2.65	2.64	2.62	2.61	2.58	2.54	2.40
cis-Stilbene	0.502	0.489	0.468	0.448	0.428	0.410	0.375
Azulene				0.18			
$Fe(DBM)_3$				5.0			

EXTINCTION COEFFICIENTS OF THE STILBENES AND CERTAIN SENSITIZERS IN METHANOL

In general, solutions about 10^{-2} M in methanol were prepared. These were diluted by use of 10 to 200 $\mu\ell$ pipets and 10 or 25 ml volumetric flasks. The absorption of the diluted solutions in one cm cells was measured at several wavelengths using a Beckman D. U. spectrophotometer. For all the compounds involved, the Beer-Lambert Law was obeyed. The results are presented in Table 8. The extinction coefficients of the stilbenes were studied more extensively since it was desirable to determine the extinction coefficient at an isosbestic point. The limits of error shown are average deviation from the mean for several different concentrations. In most cases, absorption measurements outside the limits 0.2-1.0 were discarded.

Table 8. Extinction Coefficients of the Stilbenes and Certain Sensitizers in Methanol.

Compound	Wavelength mμ	Extinction Coefficient $\times 10^{-4}$ ℓ mole^{-1} cm^{-1}
<u>trans</u>-Stilbene (grade 1)	247	0.239±0.002
	258	0.66 ±0.01
	259	0.71 ±0.003
	260	0.77 ±0.003
	261	0.84 ±0.007
	262	0.90 ±0.003
	263	0.97 ±0.007
	265	1.12 ±0.007
	266	1.20 ±0.007
	268	1.36 ±0.007
	269	1.45 ±0.007
	270	1.53 ±0.01
	275	1.95 ±0.01
	276	2.03 ±0.01
	295	2.92 ±0.02
<u>cis</u>-Stilbene	247	0.646±0.001
	258	0.89 ±0.007
	259	0.91 ±0.003
	260	0.93 ±0.007
	261	0.95 ±0.003
	262	0.96 ±0.007
	263	0.97 ±0.01
	265	0.99 ±0.01
	266	1.00 ±0.01
	268	1.02 ±0.01
	269	1.02 ±0.007
	270	1.03 ±0.007
	275	1.05 ±0.01
	276	1.05 ±0.01
	295	0.729±0.003
Benzil	247	1.59 ±0.02
	263	2.00 ±0.02
	276	1.00 ±0.005
	295	0.350±0.003

Table 8. (continued)

Compound	Wavelength mμ	Extinction Coefficient x 10^{-4} ℓ $mole^{-1}$ cm^{-1}
2-Acetonaphthone	247	4.72 ±0.005
	263	0.430±0.002
	276	0.760±0.003
	295	0.619±0.004
Benzophenone	247	1.64 ±0.005
	263	1.27 ±0.01
	276	0.520±0.004
	295	0.105±0.0005
1-Naphthaldehyde	247	1.49 ±0.01
	263	0.105±0.001
	276	0.216±0.001
	295	0.515±0.003
9-Anthraldehyde	247	3.00 ±0.04
	263	7.73 ±0.07
	276	6.14 ±0.1
	295	1.21 ±0.02
2,3-Pentanedione	263	0.0028
	276	0.0030
	295	0.0029
Phenanthrenequinone	247	2.17 ±0.02
	263	3.16 ±0.07
	276	1.03 ±0.01
	295	0.232±0.003
Fluorenone	247	5.65 ±0.1
	263	0.466±0.003
	276	0.177±0.001
	295	0.320±0.001
Acetophenone	247	1.05 ±0.005
	263	0.1086±0.0001
	276	0.0969±0.0002
	295	0.0300±0.0001

Table 8. (continued)

Compound	Wavelength mμ	Extinction Coefficient x 10^{-4} ℓ mole^{-1} cm^{-1}
9,10-Anthraquinone	247	3.89 ±0.03
	263	1.76 ±0.005
	276	0.980±0.008
	295	0.203±0.002
Mesityl oxide	263	0.117 ±0.001
	276	0.00793±0.00008
	295	0.00543±0.00003
Phorone	247	1.15 ±0.01
	263	1.940±0.003
	276	1.587±0.004
	295	0.1519±0.0007
Biacetyl[a]	263	0.00143
	276	0.00220
	295	0.00252

[a] No errors are indicated in this case because the determination of extinction coefficients was based on only one concentration of biacetyl.

SINGLET-TRIPLET ABSORPTION SPECTRA

Fluorenone

A solution of fluorenone (grade 2, 0.85 M) was prepared in freshly purified ethyl iodide. Its absorption spectrum was measured against air on the Cary 14 spectrophotometer using a 10 cm quartz cell. The spectrum showed two diffuse shoulders, one at 18,520 cm^{-1} (ε = 0.007 cm^{-1} ℓ. mole^{-1}) and the other at 19,920 cm^{-1} (ε = 0.022 cm^{-1} ℓ. mole^{-1}). The shoulder at 18,520 cm^{-1} (53 kcal/mole) was assigned to the 0-0 band for singlet-triplet absorption.

1,4-Benzoquinone

The spectrum of a saturated solution of 1,4-benzoquinone in ethyl iodide (~0.7 M) was measured as described for fluorenone. The spectrum was extremely diffuse, except for a hint of a shoulder at 17,450 cm^{-1} ($\varepsilon \approx$ 0.014 cm^{-1} ℓ. mole^{-1}). This shoulder was assumed to represent the 0-0 band for singlet-triplet absorption.

Benzanthrone

The spectrum of a saturated solution of benzanthrone in ethyl iodide (~0.1 M) was measured as described above. The solution showed absorption for frequencies higher than 17,000 cm^{-1}. There was a shoulder at 17,650 cm^{-1} ($\varepsilon \approx$ 0.04 cm^{-1} ℓ. mole^{-1}) but it will be shown later (see appendix) that it is unlikely that this shoulder represents the 0-0 band for singlet-triplet absorption.

QUANTUM YIELDS FOR SENSITIZED STILBENE ISOMERIZATIONS

The optical bench previously described was used. The 3660 Å mercury line was isolated by Corning filters C. S. 7-37 and C. S. 0-52 placed in series. In preliminary experiments, the cells employed were washed 15 x 125 mm pyrex test tubes sealed to 12/30 ground glass female joints. In later experiments, these cells were modified by inclusion of a small trap which prevented contamination of the reaction mixtures by stopcock grease from the vacuum system.

At 3660 Å , the stilbenes are transparent. In all cases the concentration of the sensitizer was sufficiently high to insure total absorption of all the incident radiation.

Tubes containing benzene solutions of either pure cis- or pure trans-stilbene and a sensitizer were degassed and sealed as described for the unsensitized photostationary state experiments (4 freeze-degas-thaw cycles). The tubes were then placed in a Beckman D. U. cell holder which was in the path of the light beam. At small time intervals, irradiation was interrupted, the contents of the tubes mixed by shaking,and the tubes placed in different positions in the cell holder before resuming irradiation. The tubes were irradiated for equal time intervals in each position of the cell holder. Total periods of irradiation were adjusted so that usually only 2-5 per cent isomer conversion was obtained. The analysis for per cent conversion was either by method 3 or method 4 described for the photostationary state experiments.

Potassium ferrioxalate actinometry was employed (39). Tubes containing solutions of potassium ferrioxalate (0.006 F) in 0.1 N sulfuric acid were irradiated prior to, during, and at the end of each experiment. The production of ferrous iron was determined by measuring the optical density of its complex with 1,10-phenanthroline at 5100 Å on a Beckman D. U. spectrophotometer. The extinction coefficient of the complex at 5100 Å was determined by the recommended procedure (39) using a standardized solution of ferrous sulfate (40). The extinction coefficient was to be $(1.132 \pm 0.003) \times 10^4$ ℓ. moles^{-1} cm^{-1}. The quantum yield for ferrous iron production at 3660 Å was taken as 1.21 (39). The higher value (1.7) reported by Lee and Seliger (41) is probably in error. The ferrioxalate actinometer has been checked against uranyl oxalate actinometry (39,42) and against benzophenone-benzhydrol actinometry (43), and in all cases the values of Hatchard and Parker appear to be correct.

RESULTS

STATIONARY STATES FOR THE STILBENES IN THE PRESENCE OF SENSITIZERS

The stationary state data are tabulated below (Table 9). Unless it is otherwise indicated, the solvent used was benzene (grade 1). The method of purification for the trans-stilbene and the sensitizer used in individual experiments is indicated by the number following the concentration. The numbers refer to the methods described in the experimental section. No number is given when only one method of purification was used. The methods of analysis, as well as the filter systems used, were described in detail in the experimental section. Briefly, the methods of analysis are: (1) ultraviolet spectroscopic analysis of total mixture, (2) separation of sensitizer by chromatography on alumina prior to ultraviolet spectroscopic analysis, (3) vapor phase chromatographic analysis of total mixture, and (4) separation of sensitizer by chromatography on alumina prior to vapor phase chromatographic analysis. The properties of the filter systems are: (1) no light was transmitted of wavelength shorter than 2900 Å, (2) only the 4045 and 4358 Å lines of mercury were transmitted, (3) and (4) mercury lines of wavelengths longer than 3300 Å were transmitted. The limits of error given are average deviations from the mean.

Table 9. Stationary States of the Stilbenes with Different Sensitizers.

Sensitizer Conc. (m/ℓ)	Total Stilbene Conc. (m/ℓ)	Initial % cis	Filter System	Temp. °C	Method of Analysis	% cis at P.S. State
Acetophenone						
0.050	0.050-2	0	1	28	1	59.3±1.0
0.0102	0.051	100	1	28	1	59.1±0.5
Benzophenone						
0.050	0.050-2	0	1	28	1	59.6±0.4
0.050	0.050	100	1	28	1	59.6±0.8
0.050	0.050-3	0	4	59	3	63.4±0.1
0.050	0.050	100	4	59	3	64.3±0.7
0.050	0.050-3	0	4	59	3	62.5±0.5
0.050	0.050	100	4	59	3	62.7±0.2
Thioxanthone						
0.050	0.050-3	0	4	28	3	61.5±0.2
0.050	0.050	100	4	28	3	58.9±0.5
Flavone						
0.050	0.050-2	0	3	28	2	61.7±0.1
0.050	0.051	100	3	28	2	61.3±0.6
Michler's Ketone						
0.050	0.050-2	0	3	28	2	63.2±0.3
0.050	0.050	100	3	28	2	62.8±0.2
4-Acetylbiphenyl						
0.050	0.050-3	0	4	28	3	64.6±0.2
0.050	0.050	100	4	29	3	65.2
0.050	0.050-3	0	4	60	4	68.7±0.6
2-Acetylfluorene						
0.050	0.050-3	0	4	31	3	65.4±0.1
0.050	0.050	100	4	31	3	66.1±0.3
0.050	0.050-3	0	4	59	3	68.2±0.3
0.050	0.050	100	4	59	3	68.7±0.4
9,10-Anthraquinone						
0.013	0.025-2	0	1	28	1	60.5±0.6
0.008	0.020-2	0	1	28	1	60.0±1.2
0.008	0.020	100	1	28	1	59.7±0.3
2-Naphthaldehyde						
0.050	0.050-2	0	3	28	2	69.7±0.3
0.050	0.051	100	3	28	2	71.3±0.3

Table 9. (continued)

Sensitizer Conc. (m/ℓ)	Total Stilbene Conc. (m/ℓ)	Initial % *cis*	Filter System	Temp. °C	Method of Analysis	% *cis* at P.S. State
2-Naphthyl Phenyl Ketone						
0.050	0.050-2	0	3	28	2	71.1±0.7
0.050	0.053	100	3	28	2	71.4±0.4
0.050	0.050-3	0	4	59	3	76.3±0.5
0.050	0.050	100	4	59	3	74.9±0.3
2-Acetonaphthone						
0.080	0.050-2	0	3	28	2	70.2±0.1
0.080	0.050	100	3	28	2	70.4±0.1
0.050	0.051	100	1	28	1	69.2±0.3
0.050	0.050-2	0	3	28	2	70.8±0.5
0.050	0.050	100	3	28	2	70.0±0.6
0.050	0.020-2	0	3	28	2	68.9±0.5
0.050	0.020	100	3	28	2	69.1±0.4
0.010	0.050-2	0	3	28	2	71.1±1.6
0.010	0.050	100	3	28	2	70.7±1.1
1-Naphthyl Phenyl Ketone						
0.050	0.050-2	0	3	28	2	73.4±0.1
0.050	0.052	100	3	28	2	73.4±0.9
1-Naphthaldehyde						
0.050	0.050	100	1	28	1	74.0±1.0
β-Naphthil						
0.050-1	0.050-2	0	2	30±2	2	85.2±0.7
0.050-1	0.051	100	2	30±2	2	84.7±0.4
0.020-2	0.050-2	0	2	28	2	84.2±0.5
0.020-2	0.050	100	2	28	2	83.9±0.8
α-Naphthil						
0.015	0.050-2	0	2	28	2	87.2±0.5
0.015	0.051	100	2	28	2	87.2±0.6
Fluorenone[b]						
0.080-2	0.050-2	0	2	28	2	86.1±1.0
0.080-2	0.050	100	2	28	2	86.0±0.2
0.050-1	0.050	0	1	28	1	86.2±0.4
0.050-1	0.055	100	1	30±2	1,2	85.4±0.4
0.027-2	0.050-2	0	2	28	2	86.5±0.4
0.027-2	0.050	100	2	28	2	86.4±0.5
0.013-2	0.050-2	0	2	28	2	86.7±0.5
0.013-2	0.050	100	2	28	2	85.6±0.4

Table 9. (continued)

Sensitizer Conc. (m/ℓ)	Total Stilbene Conc. (m/ℓ)	Initial % cis	Filter System	Temp. °C	Method of Analysis	% cis at P.S. State
Fluorenone[b] (continued)						
0.050-3	0.100	100	4	28	3	86.4±0.1
0.050-3	0.050-3	0	4	28	3	85.8±0.5
0.050-3	0.050	100	4	28	3	86.9±0.1
0.050-3	0.040-3	0	4	28	3	85.7±0.4
0.050-3	0.040	100	4	28	3	84.7±0.1
0.050-3	0.030-3	0	4	28	3	86.5±0.3
0.050-3	0.030	100	4	28	3	86.2±0.3
0.050-3	0.020-3	0	4	28	3	86.3±0.6
0.050-3	0.020	100	4	28	3	85.7±0.3
0.050-3	0.010-3	0	4	28	3	87.6±0.1
0.050-3	0.050-3	0	4	60	4	90.0±0.1
0.050-3	0.050	100	4	60	4	89.9±0.2
0.050-3	0.050-3	0	4	59	4	89.4±0.3
0.050-3	0.050	100	4	59	4	89.3±0.1
Benzil[c] (n-heptane)						
0.020	0.020-1	0	2	28	1	94.7±0.2
0.010	0.020-1	0	2	28	1	95.2±0.7
0.006	0.020-1	0	2	28	1	94.5±0.4
0.001	0.020-1	0	2	28	1	93.5±1.0
Benzil (EPA, diethyl ether, isopentane, ethanol, 5:5:2 by vol.)						
0.050	0.050-1	0	2	28	1	93.2±0.4
Benzil						
0.050	0.050-1	0	2	28	1	90.8±1.0
2,3-Pentanedione						
0.051	0.050-1	0	2	28	1	87.4±0.6
2,3-Pentanedione (EPA)						
0.051	0.050-1	0	2	28	1	91.5±1.0
Biacetyl						
0.201	0.050-2	0	1	28	1	86.8±0.4
1,4-Naphthoquinone[d]						
0.050	0.050-2	40	2	28	2	59.2±0.5
0.050	0.050-2	80	2	28	2	60.9±0.3

Table 9. (continued)

Sensitizer Conc. (m/ℓ)	Total Stilbene Conc.(m/ℓ)	Initial % cis	Filter System	Temp. °C	Method of Analysis	% cis at P.S.State
Duroquinone						
0.080	0.050-3	0	4	28	4	65.8±0.8
0.080	0.050	100	4	28	4	65.1±0.2
0.050	0.050-2	0	2	28	2	71.4±0.2
0.050	0.050	100	2	28	2	71.0±0.5
0.050	0.050-3	0	4	28	4	71.7±0.1
0.050	0.050	100	4	28	4	72.8±0.4
0.020	0.050-3	0	4	28	4	75.2±0.8
0.020	0.050	100	4	28	4	74.2±0.4
Pyrene						
0.050	0.050-3	80	1	28	3	91.5±0.2
0.050	0.050	100	1	28	3	91.5±0.2
0.020	0.050-3	80	1	28	3	90.8±0.3
0.020	0.050	100	1	28	3	91.3±0.1
0.010	0.050-3	80	1	28	3	87.5±0.1
0.010	0.050	100	1	28	3	88.2±0.2
1,2-Benzanthracene[e]						
0.050	0.050-3	40	4	28	3	80.4±0.3
0.050	0.050	80	4	28	3	79.8±0.1
0.020	0.050-3	40	4	28	3	87.6±0.2
0.020	0.050-3	80	4	28	3	88.2±0.2
0.010	0.050-3	40	4	28	3	90.7±0.1
0.010	0.050-3	80	4	28	3	90.3±0.1
Benzanthrone[f]						
0.051	0.050-1	0	2	28	2	42.1±0.9
0.050	0.051	100	2	28	2	40.9±1.0
0.020	0.050-2	20	2	28	2	62.2±0.5
0.020	0.050-2	60	2	28	2	60.9±0.4
0.015	0.050-1	0	2	28	2	66.8±0.8
0.015	0.050	100	2	28	2	65.9±0.8
0.010	0.050-2	20	2	28	2	72.0±0.5
0.010	0.050-2	60	2	28	2	70.6±0.2
Acridine						
0.050	0.050-3	40	4	28	3	38.5±0.2
0.050	0.050-3	80	4	28	3	38.2±0.1
0.020	0.050-3	40	4	28	3	55.4±0.1
0.020	0.050-3	80	4	28	3	55.4±0.1
0.010	0.050-3	40	4	28	3	64.8±0.3
0.010	0.050-3	80	4	28	3	64.9±0.5

Table 9. (continued)

Sensitizer Conc. (m/ℓ)	Total Stilbene Conc. (m/ℓ)	Initial % cis	Filter System	Temp. °C	Method of Analysis	% cis at P.S. State
3-Acetylpyrene						
0.080	0.050-2	0	3	28	2	29.2±0.5
0.080	0.050	100	3	28	2	29.3±0.0
0.050	0.050-2	0	3	28	2	39.8±0.7
0.050	0.053	100	3	28	2	39.6±0.3
0.020	0.050-2	0	3	28	2	55.0±0.1
0.020	0.050	100	3	28	2	55.2±0.1
0.010	0.050-2	0	3	28	2	65.0±0.9
0.010	0.050	100	3	28	2	64.1±0.6
1,4-Benzoquinone[g]						
0.080	0.050-2	0	2	28	2	19.6±0.8
0.080	0.054-2	65	2	28	2	17.8±0.7
0.050	0.050-2	0	2	28	2	20.6±0.9
0.050	0.051-2	69	2	28	2	20.4±1.7
0.030	0.050-2	10	2	28	2	22.6±0.8
0.030	0.050-2	40	2	28	2	22.6±0.5
0.020	0.050-2	20	2	28	2	29.7±0.6
0.020	0.050-2	50	2	28	2	30.5±1.0
0.010	0.050-2	30	2	28	2	35.0±1.0[h]
0.010	0.050-2	50	2	28	2	
0.005	0.050-2	40	2	28	2	39.3±0.3[h]
0.005	0.050-2	60	2	28	2	
0.030	0.050-2	10	2	28	2	24.2±0.7
0.020	0.020-2	20	2	28	2	22.8±0.4
0.020	0.020-2	50	2	28	2	23.1±1.3
0.020	0.015-2	20	2	28	2	23.0±1.0
0.020	0.105-2	50	2	28	2	23.2±2.5
0.020	0.010-2	20	2	28	2	22.4±1.0
0.020	0.010-2	50	2	28	2	20.8±1.0
Phorone[i]						
0.100	0.050-2	0	1	28	1	76.7±2.4
0.101	0.050	100	1	28	1	79.8±3.6
Mesityl oxide[j]						
0.406	0.050-2	0	1	28	1	70.6±0.6
Eosin[k] (benzene-diethyl ether, 1:1 by volume)						
<0.050(sat'd)	0.050-3	0	4	31.5	3	0.2±0.1
<0.050(sat'd)	0.050	100	4	31.5	3	0.2±0.1

Table 9. (continued)

Sensitizer Conc. (m/ℓ)	Total Stilbene Conc. (m/ℓ)	Initial % *cis*	Filter System	Temp. °C	Method of Analysis	% *cis* at P.S. State
9,10-Dibromoanthracene						
0.010	0.050-3	0	4	28	3	0.2±0.0
0.010	0.050	100	4	28	3	0.2±0.0

a. Irradiation at 60° led to decomposition of thioxanthone as evidenced by disappearance of yellow color from the solutions.
b. Fluorenone interfered slightly with analysis 3 of the stilbenes.
c. See page 65 for further comments on data involving benzil in *n*-heptane.
d. See page 65 for further documentation of this photostationary state.
e. A white photoproduct precipitated from solution. Since this is probably 1,2-benzanthracene dimer (44), the initial concentration of benzanthracene should be taken as upper limits.
f. After chromatography on alumina, eluents for first two benzanthrone runs were pale yellow.
g. After chromatography and analysis of the tubes for the last six entries for 1,4-benzoquinone, it was shown that as much as 17 to 30 per cent of the initial stilbene concentration could not be accounted for. This may be due either to addition of 1,4-benzoquinone to stilbene (45) or to preferential loss of *cis*-stilbene during the evaporation of solvent after chromatography on alumina (see page 44).
h. This value was obtained by extrapolation.
i. See page 66 for further comments on this result.
j. See page 66 for additional information on mesityl oxide.
k. The vapor phase chromatographic traces showed two small peaks, rather than one, where *cis*-stilbene should appear.

Further data on certain sensitizers will be presented individually.

Benzil

It was found that for the first three experiments described in Table 9 for the benzil sensitized stilbene isomerization in n-heptane, the stationary state had been attained at the end of 1.8 hours of irradiation. A side reaction, probably addition of benzil to stilbene (46), was competing, as evidenced by drop of absorption at the isosbestic wavelength (263 mμ) for the stilbenes. The effect of the side reaction on the analysis is demonstrated in Table 10.

Table 10. Effect of Side Reaction on Calculation of Stationary States for Benzil Sensitized Stilbene Isomerization.

Time (hours)	Apparent Total Stilbene Conc. (m/ℓ)			% *cis* Calculated		
Experiment	1	2	3	1	2	3
0	0.0204	0.0199	0.0200	1.5±1.5	0.5±0.5	1.2±0.2
1.8	0.0194	0.0195	0.0199	94.7±0.2	95.2±0.7	94.5±0.4
2.8	0.0190	0.0190	0.0192	92.7±0.5	93.0±0.1	93.0±0.1
3.5	0.0184	0.0184	0.0186	92.0±1.0	93.2±0.4	92.3±0.6

The fourth benzil experiment in n-heptane was not complicated as above. No change in the apparent total stilbene concentration was observed during a 2 hour irradiation period.

1,4-Naphthoquinone

Because of the special place of the point for 1,4-naphthoquinone on the stilbene curve (see discussion) and since the dimerization of 1,4-naphthoquinone (44) or its addition to stilbene (45) might produce a higher energy sensitizer, it was necessary to further establish this stationary state. Two experiments were carried out which were identical to the experiments for 1, 4-naphthoquinone described in Table 9, except that the initial stilbene compositions were 60 and 70 per cent *cis* isomer, respectively. Samples of the two solutions were irradiated in parallel for short time periods. The results are shown in Table 11. The trends observed are in excellent agreement with the values shown in Table 9.

Table 11. The Stilbene Stationary State in the Presence of 1, 4-Naphthoquinone.

Time (minutes)	% *cis*	% *cis*
0	60	70
6	60.6±0.4	68.9±0.2
11	60.7±0.2	68.0±0.1
15	60.5±0.0	67.4±0.3

Phorone and Mesityl Oxide

The significance of the data shown in Table 9 for the phorone and mesityl oxide sensitized stilbene isomerization is not clear at this time. The rates of isomerization were very slow in each case, and since only the 2900 Å cut-off filter was used, it is possible that the observed isomerization was due to direct absorption of light by the stilbenes. Furthermore, the ultraviolet absorption measurements indicated that products from side reactions interfered with the analysis for the stilbenes.

The presence of mesityl oxide in high concentration does not appear to affect the rate of the benzophenone or the 9, 10-anthraquinone sensitized stilbene isomerizations; however, it seems to affect the composition at the stationary state. This effect is not understood at present, but it may be an artifact of the method of analysis. Data are shown in Table 12. The rates for stilbene isomerization in the presence of and in the absence of mesityl oxide for sensitization by 9, 10-anthraquinone are compared in Table 13. Under

Table 12. Sensitized Isomerization of the Stilbenes in the Presence of Mesityl Oxide (0.40 M in benzene).

Sensitizer Conc.(m/ℓ)	Total Stilbene Conc.(m/ℓ)	Initial % *cis*	Filter System	Temp. °C	Method of Analysis	% *cis* at P.S.State
9, 10-Anthraquinone						
0.008	0.020-2	0	1	28	1	53.2±1.1
Benzophenone						
0.025	0.025-2	0	1	28	1	62.1±1.2

Table 13. Effect of Mesityl Oxide on Rate of 9, 10-Anthraquinone Sensitized Stilbene Isomerization.[a]

Time (hours)	% cis(no mesityl oxide)	% cis(0.400 M mesityl oxide)
0	0	0
0.33	50.0±0.5	32.5±0.1
0.66	59.4±1.4	47.2±0.9
1.00	59.1±0.4	53.7±1.0
3.00	61.4±1.2	52.8±1.3

a. 9, 10-Anthraquinone (0.008 M) and *trans*-stilbene (0.020 M) in benzene solution. Filter system 1, analysis 1, and 28° temperature were used.

similar conditions (0.400 M in mesityl oxide), in the absence of 9,10-anthraquinone, the stationary state for the stilbenes is not attained after 15 hours of irradiation. It may be reasonable to assume that the triplet state energy of mesityl oxide is lower than those of benzophenone or 9,10-anthraquinone. This assumption leads to two conclusions. The first is that intersystem crossing is not an efficient process in mesityl oxide, and the second is that the triplet state of mesityl oxide, when produced indirectly, can effect the isomerization of the stilbenes.

Santonin and 4-Methyl-4-dichloromethylcyclohexadienone

Irradiation of either santonin (0.05 M) or 4-methyl-4-dichloromethylcyclohexadienone (0.05 M) in the presence of cis- or trans-stilbene (0.05 M) for 5 hours (filter system 4) led to essentially no isomerization of the stilbenes (method 3). Furthermore, analysis of one of the irradiated santonin samples by Mr. M. H. Fisch, showed that the presence of stilbene apparently did not affect the course of the photodecomposition of santonin (47).

Benzophenone and 2,3-Pentanedione

An experiment was carried out in which benzophenone (0.050 M) and 2,3-pentanedione (0.054 M) were used simultaneously as sensitizers for the isomerization of trans-stilbene (0.050-1 M). Irradiation was carried out at 28° using the 2900 Å cut-off filter (filter system 1). Analysis of the mixtures was by ultraviolet spectroscopy (method 1). As expected, the observed stationary state (81±1.5% *cis*) is bracketed by the stationary state for benzophenone (59.6±0.8% *cis*) and the stationary state for 2,3-pentanedione (87.4±0.6% *cis*).

Phenanthrenequinone

A stationary state was not obtained for phenanthrenequinone because the formation of adduct with stilbene (48) prevented analysis by ultraviolet spectroscopy. However, the results are of interest since they indicate that the rate of formation of adduct is the same from either stilbene isomer. The rate of the side reaction is reflected by the apparent concentration of stilbene that is calculated from the absorption at the isosbestic point (Table 14).

Table 14. Rate of Formation of Adduct between Phenanthrenequinone and the Stilbenes.

Initial Concentrations		
Phenanthrenequinone:	0.020 M	0.020 M
Stilbene :	0.020 M *trans*	0.020 M *cis*
Time(hours)	Apparent Total Stilbene Concentration	
0	0.0199	0.0195
1.00	0.0163	0.0163
3.66	0.0153	---
6.25	0.0148	0.0147

Chelates, Azulene

Ferric dipivaloylmethide and chromium dipivaloylmethide did not photosensitize the isomerization of the stilbenes (49). Results comparing rate of isomerization of trans-stilbene (0.05 M) in the absence or presence of the chelates (0.005 M)are shown in Table 15. It appears that the effect of the chelates can be attributed to internal filtering of the unsensitized isomerization.

Table 15. Rate of Isomerization of trans-Stilbene in Presence of Chelates (reported in % cis)

Time (hours)	Blank	$Fe(DPM)_3$	$Cr(DPM)_3$
0.50	6.5	6.0	6.0
1.03	12.5	10.0	9.5
2.00	21.0	19.0	14.5

The same result was obtained when azulene was used as the photosensitizer.

SENSITIZED ISOMERIZATION OF THE STILBENES IN THE PRESENCE OF AZULENE

Data for experiments in which azulene was included in the reaction mixtures with various sensitizers are shown in Table 16. In all cases benzene solutions of the sensitizer (0.020 M) and the stilbenes (0.050 M) were used. The "merry-go-round" apparatus was employed and unless it is otherwise indicated, filter solution 2 (page 41) and method of analysis 2 (page 43) were employed. The temperature of the reaction mixtures was kept at 28° during the irradiation period.

Table 16. Stationary States for the Stilbenes with Various Sensitizers in the Presence of Azulene.

Sensitizer	Azulene Conc. (m/ℓ)	Initial % cis	% cis at P.S. State
9,10-Anthraquinone	0.005	0	45.6±0.4
	0.005	100	47.4±0.5
	0.010	0	38.8±0.7
	0.010	100	38.8±0.1
Benzil	0.005	0	87.4±0.1
	0.005	100	87.6±0.1
	0.010	0	82.2±1.0
	0.010	100	83.6±0.4
Fluorenone	0.0039	0	79.9±0.2
	0.0039	100	80.1±0.5
	0.010	0	71.6±0.2
	0.010	100	71.6±0.4
Benzanthrone	0.010	0)	55.0±1.0[a]
	0.010	100)	
Benzophenone[b]	0.005	0	48.3±0.2
	0.005	100	47.8±0.2
	0.010	0	39.5±1.0
	0.010	100	40.5±0.2

a. This value obtained by extrapolation.

b. In this case filter system 1 and analysis 3 were used. It was found that ultraviolet spectroscopic analysis gave erratic results, possibly because of some photodecomposition of azulene. Only in the benzophenone experiments was azulene absorbing a major portion of the incident light.

STATIONARY STATES FOR THE SENSITIZED ISOMERIZATION OF 2,3-DIPHENYLBUTENE-2

Photostationary states were determined for the isomerization of 2,3-diphenylbutene-2 in the presence of three sensitizers. The stationary states were approached starting from the pure trans isomer. Three samples of each solution were irradiated for long time intervals (20.5, 32.5, and 40.5 hours, respectively). Analysis was as described for the stilbenes (method 4, page 44). It involved chromatography of the reaction mixtures on alumina prior to vapor phase chromatographic analysis. For each sensitizer the stationary state had been attained during the shortest irradiation period. The uranium glass filter and the merry-go-round apparatus were used. The solvent used was benzene (grade 1) and the temperature during irradiation was 28°. Results are shown in Table 17.

Table 17. Stationary States of the 2,3-Diphenylbutene-2's with Different Sensitizers.

Sensitizer Conc. (m/ℓ)	Initial trans-2,3-Diphenylbutene-2 Conc. (m/ℓ)	% cis at P. S. State
Benzophenone 0.050	0.050	24.7±0.2
Fluorenone 0.050-3	0.050	4.08±0.06
9,10-Dibromoanthracene 0.010	0.050	31.0±0.5

ON THE FORMATION OF GROUND STATE COMPLEXES BETWEEN SENSITIZERS AND THE STILBENES

It was found that whereas a solution of chloranil (0.05 M) in benzene is yellow, the solution becomes red in the presence of trans-stilbene (0.05 M) and orange in the presence of cis-stilbene (0.05 M). This striking evidence in favor of ground state complexes between chloranil and the stilbenes led to the suspicion that complexes may also form between the stilbenes and some of the sensitizers. This possibility was examined in only two cases. It was found that under the conditions of sensitized isomerizations, trans-stilbene forms a weak complex with 1,4-benzoquinone, but does not complex with benzanthrone. The results that led to these conclusions are tabulated below. Spectra were measured with the Cary 14 spectrophotometer.

Table 18. Apparent Extinction Coefficients of 1,4-Benzoquinone in the Presence of trans-Stilbene in Benzene.

trans-Stilbene Conc. (m/ℓ)	1,4-Benzoquinone Conc. (m/ℓ)	Apparent Extinction Coefficient 3900Å	4100Å	4300Å	4550Å	4800Å
0.0866	0	0	0	0	0	0
0	0.0702	8.55	13.2	18.9	20.4	11.4
0.0433	0.0351	14.8	18.2	21.9	21.8	12.2
0.0130	0.0105	10.3	14.5	19.8	20.9	11.6
0.0606	0.0211	17.2	20.0	23.2	22.2	12.3

Clearly, dependence of the apparent extinction coefficient on trans-stilbene concentration is observed in the case of 1,4-benzoquinone but not in the case of benzanthrone.

Table 19. Apparent Extinction Coefficients of Benzanthrone in the Presence of trans-Stilbene in Benzene.

trans-Stilbene Conc. (m/ℓ)	Benzanthrone Conc. (m/ℓ)	Apparent Extinction Coefficient			
		4400Å	4425Å	4450Å	4500Å
0	0.0250	33.2	19.7	11.6	4.44
0.0126	0.0250	33.2	19.7	11.6	4.48
0.0505	0.0250	33.4	19.7	11.6	4.48
0.0619	0.0250	33.3	19.8	11.7	4.44

The fact that change of either stilbene or sensitizer concentration does not affect the stationary state of the stilbenes when 2-acetonaphthone, benzil, or fluorenone are used as sensitizers (see Table 9) indicates that ground state complexes are not involved in these three cases.

STATIONARY STATES FOR THE DIRECT PHOTOISOMERIZATION OF THE STILBENES

Photostationary states for the unsensitized isomerization of stilbene in the presence or absence of quenchers are shown in Table 20. As was described in the experimental part, the filter system used for the experiments described in the first four entries of Table 20 was not very satisfactory. For these experiments the incident light was not monochromatic. However, since irradiation was mainly with

Table 20. Stationary States for the Isomerization of the Stilbenes by Direct Light Absorption (3130 Å) in the Absence or Presence of Quenchers in Benzene-2.

Quencher	Quencher Conc. (m/ℓ)	Total Stilbene Conc. (m/ℓ)	Initial % cis	Final % cis
None	0	0.0500-3	0	84.7±0.4
	0	0.0500	100	83.1±1.0
	0	0.0010-3	0	92.2±1.2
	0	0.0010	100	91.7±1.0
	0	0.0016	75-3	89.6±0.5
	0	0.0016	100	89.4±0.1
Azulene	0.004	0.0016	75-3	88.4±0.2
	0.004	0.0016	100	88.4±0.1
	0.008	0.0016	75-3	87.9±0.5
	0.008	0.0016	100	87.1±0.5
	0.012	0.0016	75-3	87.1±0.2
	0.012	0.0016	100	86.9±0.2
	0.020	0.0016	75-3	85.3±0.5
	0.020	0.0016	100	85.6±0.1
$Fe(DBM)_3$	0.0016	0.0016	75-3	89.8±0.4
	0.0024	0.0016	75-3	89.5±0.2
	0.0024	0.0016	100	89.2±0.1

the 3130 Å mercury line, the effect of stilbene concentration on the stationary state is, at least qualitatively, significant. The ultraviolet spectroscopic analysis used for the first four runs in Table 20 ruled out the possibility that phenanthrene formation might occur in the absence of oxygen in solution.

THE DISAPPEARANCE OF TRANSIENT(S) FORMED UPON DIRECT IRRADIATION OF THE STILBENES

As is shown in Figure 3 (see also Table 5), the disappearance of the transient obeys first order kinetics at least for the first 70 minutes after irradiation was interrupted. The rate of disappearance of color appears to increase at the lower concentration of transient. The initial rate constant for transient disappearance is 5.4×10^{-3} min^{-1} at about 30° (half-life about 128 minutes). The rate constant increases to 7.2×10^{-3} min^{-1} at the later stages of the reaction. This increase might be attributed to experimental uncertainty.

Very qualitative measurements were made to determine the effect of azulene on the rate of disappearance of the transient(s). The data were shown in Table 6. Their qualitative nature is mainly due to the very small concentration of transient formed under the conditions of the experiments involved (see Table 6). As is shown in Figure 4, the data do not satisfy first order kinetics. Perhaps the only meaningful conclusion that should be drawn from these results is that the disappearance of transient is faster in the presence of azulene.

The effect of azulene on the absolute concentration of transient(s) is easily calculated. Since the transient forms only from cis-stilbene, its concentration should be proportional to the fraction of light

Fig. 3. Rate of Disappearance of Transient.

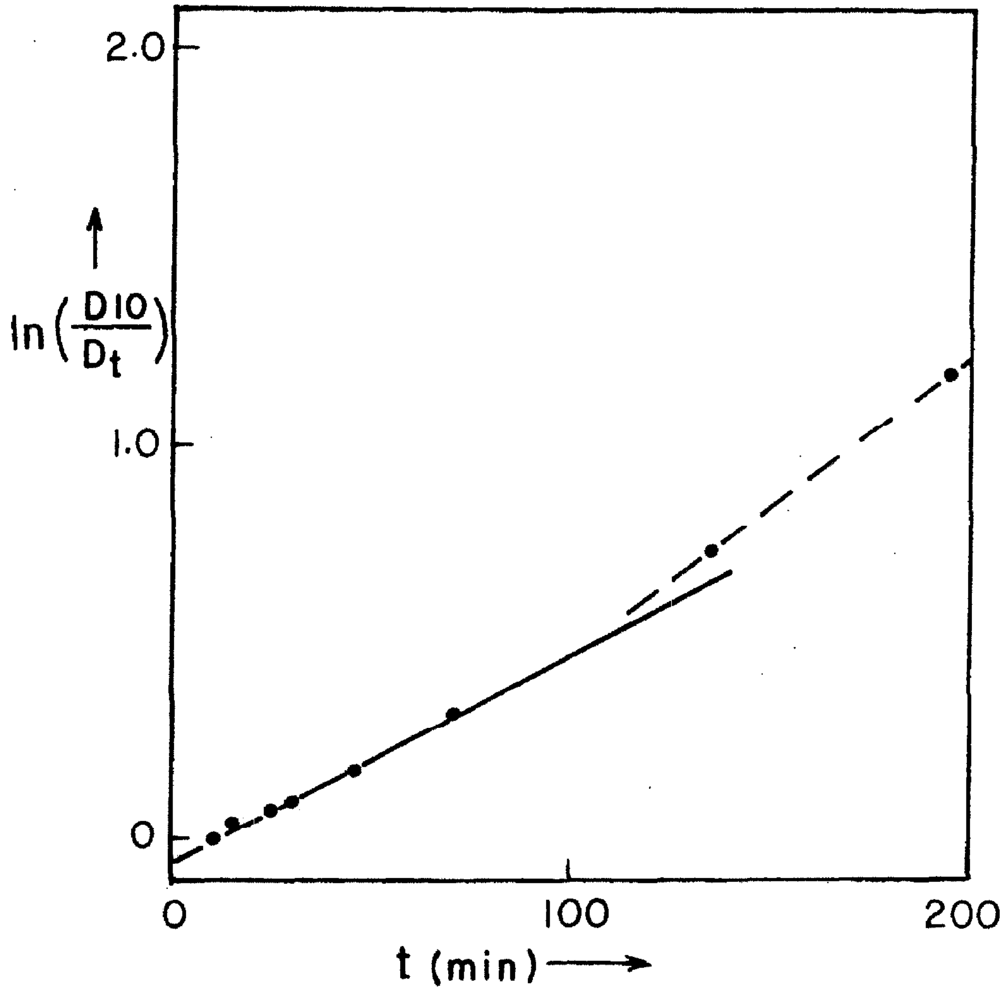
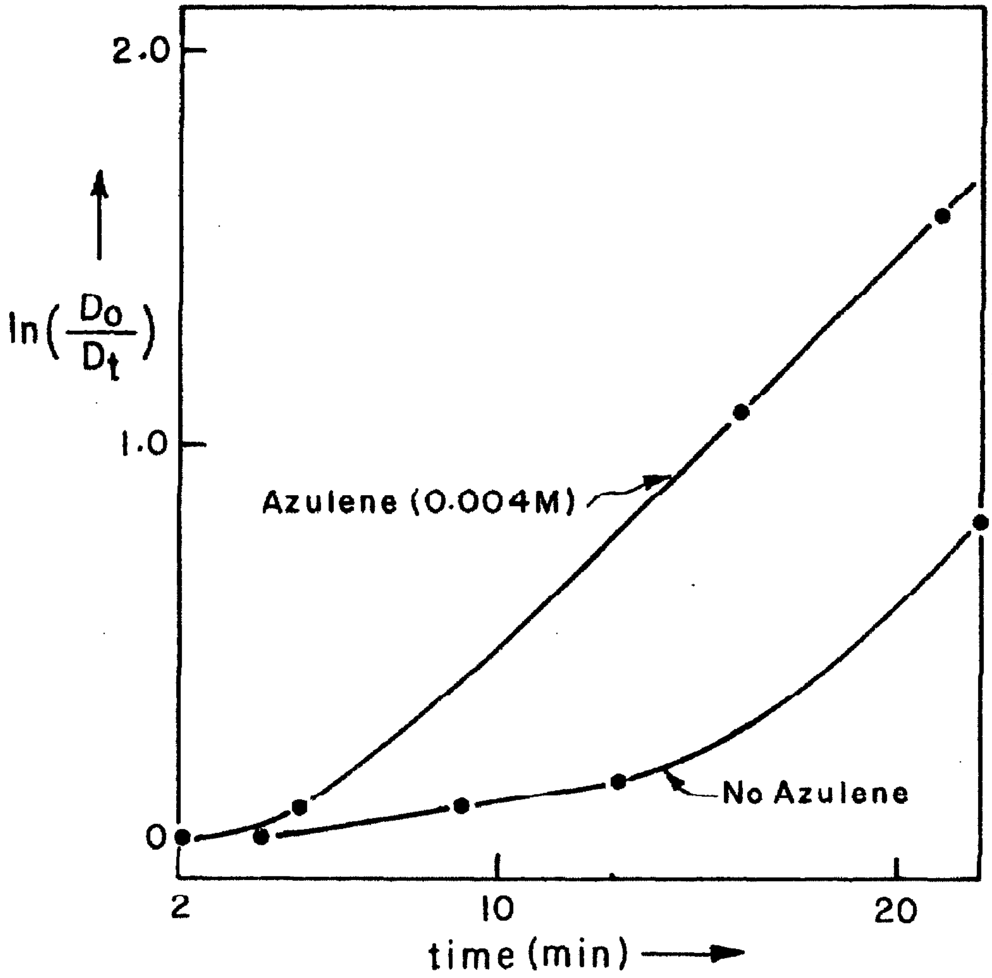


Fig. 4. Decay of Transient Absorption at 4500 Å.



absorbed by cis-stilbene. Using the extinction coefficients at 3130 Å (Table 7) and the concentrations of the components of each solution (Table 20) at the stationary state, it is calculated that in the presence of azulene 0.59 as much transient(s) absorption should be observed as is observed in the absence of azulene. Immediately after irradiation was interrupted, the observed ratio of optical densities at 4500 Å was actually 0.83. The steady state concentration of transient(s) appears to have increased by 40% when azulene (0.004 M) was added to the reaction mixture. Despite the crudity of this measurement, this increase appears to be outside experimental error.

QUANTUM YIELDS FOR SENSITIZED STILBENE ISOMERIZATION

The results from preliminary experiments are very approximate. The reaction mixtures for these experiments were not satisfactorily protected from diffuse daylight. As a result, an indeterminate amount of isomerization occurred prior to irradiation on the optical bench. The data are shown in Table 21. The values should be regarded as high estimates (by as much as 50%) of the correct value.

In the last set of experiments, extreme care was taken to insure that exposure of the solutions to light was only during the desired period of irradiation. The data are shown in Tables 22 and 23.

Table 21. Preliminary Quantum Yields (φ) for the Sensitized Stilbene Isomerization.

Sensitizer	Sensitizer Conc. (m/ℓ)	Stilbene Conc. (m/ℓ)	$\varphi_{c\to t}$	$\varphi_{t\to c}$
Fluorenone	0.050	0.050	0.4	
	0.050	0.050-3		0.5
Benzil	0.050	0.050	0.4	
	0.050	0.050-3		0.5
Benzophenone	0.050	0.050	0.5	
	0.050	0.050-3		0.5
Flavone	0.050	0.050	0.4	
	0.050	0.050-3		0.4
2-Naphthyl	0.050	0.050	0.5	
Phenyl Ketone	0.050	0.050-3		0.4

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Table 22. Quantum Yields for the Benzophenone Sensitized Isomerization of trans-Stilbene in Benzene (grade 2).

Benzophenone Conc. (m/ℓ)	trans-Stilbene Conc. (m/ℓ)	Conversion (%)	$\varphi_{t\to c}$
0.050	0.050-3	2.39	0.41±0.02
0.050	0.030-3	2.39	0.41±0.01
0.050	0.010-3	5.14	0.44±0.01
0.050	0.005-3	5.30	0.45±0.02
0.050	0.001-3	8.77	0.48±0.01

The errors reflect only the uncertainty in the vapor phase chromatographic analysis. The initial content of cis isomer in the trans stock solution was shown to be 0.09% of the total stilbene concentration, and the content of trans isomer in the cis stock solution was found to be 0.15% of the total.

Table 23. Quantum Yields for the Fluorenone Sensitized Isomerization of the Stilbenes in Benzene (grade 2)

Fluorenone Conc. (m/ℓ)	Stilbene Conc. (m/ℓ)	Conversion (%)	$\varphi_{t\rightarrow c}$	$\varphi_{c\rightarrow t}$
0.050	0.100	1.21	0.42±0.00	
0.050	0.050	2.60	0.44±0.00	
0.050	0.050	1.44		0.25±0.02
0.050	0.040	1.88	0.43±0.02	
0.050	0.030	2.53	0.43±0.01	
0.050	0.030	1.22		0.21±0.01
0.050	0.020	2.28	0.39±0.01	
0.050	0.020	2.43		0.20±0.003
0.050	0.010	3.87	0.34±0.00	
0.050	0.005	4.72	0.40±0.01	
0.050	0.001	5.19	0.28±0.01	

RESULTS AND DISCUSSION

The formation and the quenching of stilbene triplet states by energy transfer were used in an attempt to elucidate the mechanism of cis-trans photoisomerization in this system. An important consequence of this study is that it led to a better understanding of triplet excitation transfer processes.

It was shown that cis-trans isomerization can be effected by irradiation of solutions containing either stilbene isomer in the presence of suitable energy donors (photosensitizers). Donors were a series of compounds which after excitation by absorption of light decay, at least in part, by way of triplet states. In the sensitized isomerization experiments the light was carefully filtered so that in most cases it was absorbed only by the sensitizer. Implicit in this statement is the best argument against the involvement of singlet energy transfer to account for the results. Even in the few cases where a small fraction of the exciting quanta absorbed by the sensitizers had sufficient energy to effect the $S_0 \rightarrow S_1$ transition in the stilbenes, efficient transfer of singlet energy can be ruled out. After internal conversion to the 0-vibrational level of the lowest singlet state of the sensitizer, singlet energy transfer to either trans- or cis-stilbene would be endothermic in all cases by 5 kcal per mole or more. These arguments suggest strongly that the mechanism of the sensitized isomerization involves as a key step transfer of triplet excitations from the excited donors to the stilbenes.

The behavior of different sensitizers was characterized by the determination of the photostationary [*cis*]/[*trans*] ratio obtained in their presence. In most cases this ratio appears to depend mainly on the triplet state energy of the sensitizer (see appendix). When the energy of the sensitizer was below 53 kcal per mole the stationary state was shown to be a function of the concentration of the sensitizer. The following mechanism accounts for most of the data. Asterisks indicate excited triplet states.

$$S^* + \underline{\text{trans}} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} S + \underline{\text{trans}}^* \qquad (1)^{\dagger}$$

$$S^* + \underline{\text{cis}} \xrightarrow{k_2} S + \underline{\text{cis}}^* \qquad (2)$$

$$S^* + \underline{\text{cis}} \xrightarrow{k_3} S + \underline{\text{trans}}^* \qquad (3)$$

$$\underline{\text{cis}}^* \xrightarrow{k_4} \underline{\text{trans}^*} \qquad (4)$$

$$\underline{\text{trans}}^* \xrightarrow{k_5} \underline{\text{trans}} \qquad (5)$$

$$\underline{\text{trans}}^* \xrightarrow{k_6} \underline{\text{cis}} \qquad (6)$$

Reactions 1, 2, and the reverse of 1 are of the type commonly suggested for energy transfer (50). The excitation and deexcitation acts in 1 and 2 involve the states which are spectroscopically observed in $T_1 \rightarrow S_0$ emission (phosphorescence) and $S_0 \rightarrow T_1$ absorption. Occurrence of 4 is suggested by the observation that excitation of either isomeric stilbene produces an excited state which can be

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† Numbers of equations in this discussion should not be confused with those used in the introduction.

deactivated to trans-stilbene by transfer of electronic energy to a suitable acceptor (low energy sensitizer or azulene, vide infra).

The transformation of the cis triplet to a triplet of different geometry must be fast since the reverse of reaction 2 was not observed even in the most favorable cases.

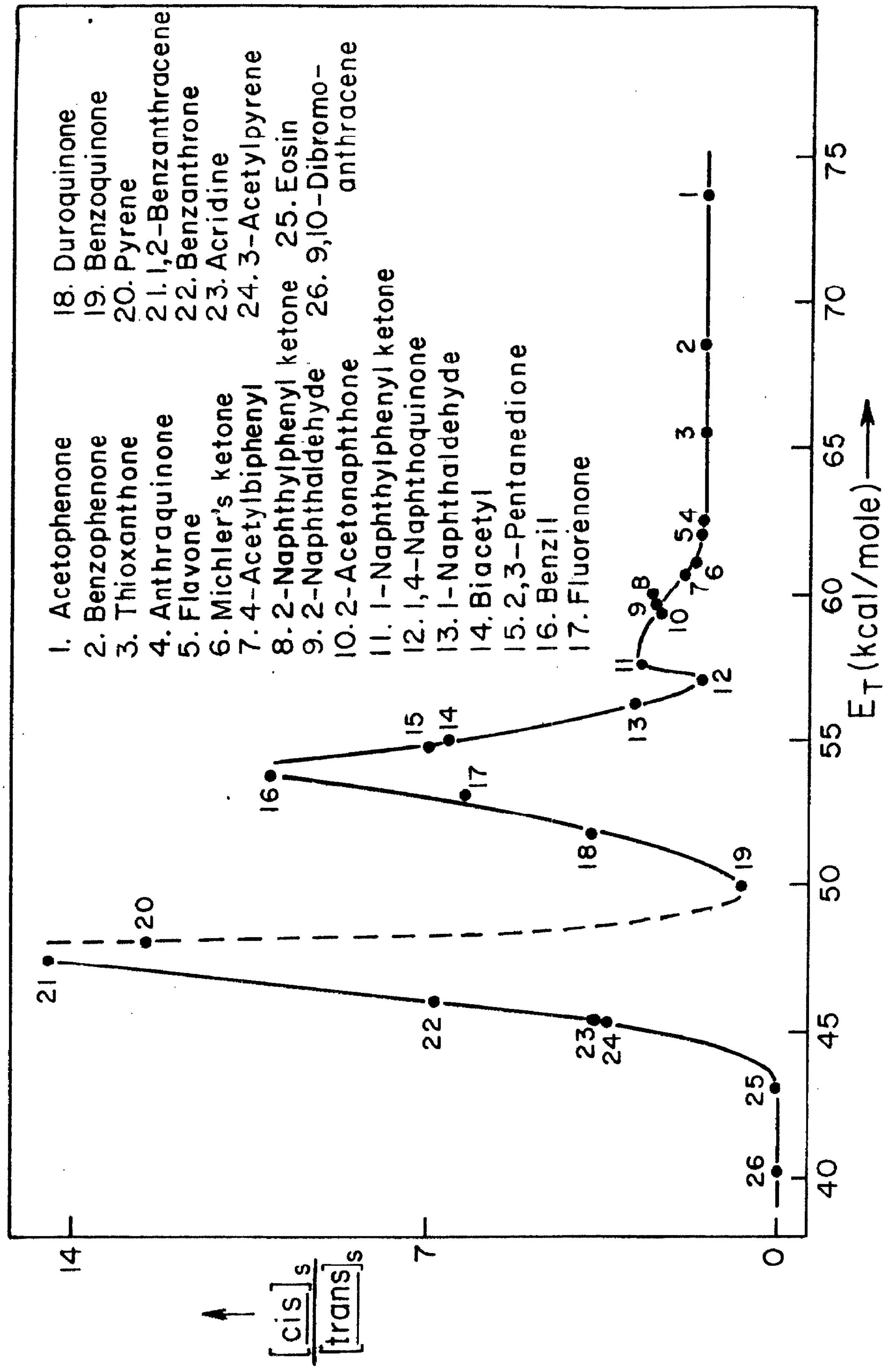
Reaction 5 is an ordinary radiationless transition. Reaction 6 implies that isomerization occurs in the vibrationally excited S_0 states formed by intersystem crossing from the trans triplet. This reaction is not demanded by the data and will be discussed at some length later.

The most startling reaction in the mechanism under consideration is 3. This process must involve some transformation of the acceptor that does not conform to the Franck-Condon Principle. This nonvertical excitation of cis-stilbene is demanded by the data. cis-Stilbene is a moderately effective acceptor of energy from sensitizer triplets which do not have sufficient energy to promote the substrate to its spectroscopic state.

The dependence of the composition of the photostationary state on the triplet state energy of the sensitizer is shown in Figure 5. Since results with sensitizers having excitation energies less than 53 kcal per mole are sensitive to the concentration of the sensitizer, the data plotted are extrapolated values for infinite dilution.

If reaction 3 is omitted, the mechanism predicts the following photostationary condition:

Fig. 5. Photosensitized Isomerization of the Stilbenes.



$$\frac{[\text{cis}]_s}{[\text{trans}]_s} = \frac{k_1 k_6}{k_2 (k_5 + k_{-1}[S])} \qquad (7)$$

The results in Figure 5 obey the condition $k_5 >> k_{-1}[S]$. Under this condition, 7 reduces to 8 .

$$\frac{[\text{cis}]_s}{[\text{trans}]_s} = \frac{k_1 k_6}{k_2 k_5} \qquad (8)$$

Variation in the stationary state ratio as the sensitizer is changed should depend on the values of k_1/k_2.

The $S_0 \rightarrow T_1$ absorption spectra of cis- and trans-stilbene have been measured. From the spectra maximum energies for the 0-0 bands of the two isomers are estimated to be 57 and 50 kcals per mole, respectively.* Since energy transfers exothermic by more than 3-5 kcal per mole appear to be diffusion controlled (50,51), the ratio k_1/k_2 should be unity for sensitizers with excitation energies greater than about 62 kcal per mole. For these sensitizers the composition of the stationary state should be determined only by the decay processes of the stilbene triplets. Figure 5 shows that this expectation is borne out, since for sensitizers with excitation energies between 62.4 and 74 kcal per mole, the stationary state is independent

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* As will be shown later, the chemical evidence presented here suggests that the 0-0 band of trans-stilbene is actually at 47±1 kcal per mole. If this is the case, then the lowest band observed spectroscopically is the 0-1 band.

of the nature of the sensitizer.

One would expect the value of k_1/k_2 to increase as the energy of the sensitizer is lowered toward, and falls below, 57 kcal per mole. This accounts for the production of cis-rich mixtures with sensitizers having excitation energies of 54-62 kcal per mole. If energy transfer always occurred such that only the corresponding spectroscopic "planar" triplet were formed from each stilbene, the value of k_1/k_2 should continue to increase as the energy of the sensitizer falls below 54 kcal per mole. However, Figure 5 indicates that the value k_1/k_2 apparently decreases for sensitizers with energies below 54 kcal per mole, increases to a new maximum at about 48 kcal per mole, and finally becomes immeasurably small with sensitizers of still lower energy. It is suggested that reaction 3, or some other process requiring less energy that the transition to the spectroscopic cis triplet, must become important with sensitizers of lower energy than 54 kcal per mole. Since the ground state of cis-stilbene is unstable with respect to that of the trans isomer by 6 kcal per mole (13), in any pair of processes in which the two isomers undergo transitions to a common state, the reaction involving the cis isomer will be favored on energetic grounds. Inclusion of step 3 in the mechanism leads to the rate law shown in equation 9.

$$\frac{[\underline{cis}]_s}{[\underline{trans}]_s} = \frac{k_1k_6}{(k_2+k_3)(k_5+k_{-1}[S])} \qquad (9)$$

With high energy sensitizers, k_1 and k_2, the rate constants for energy transfer with vertical excitation of the acceptor, have the magnitude for diffusion-controlled processes and are larger than k_3. The value of k_2 falls off as the excitation energy of sensitizers approaches and falls below the $S_0 \rightarrow T_1$ excitation energy of *cis*-stilbene. As the energy of the sensitizers is lowered further, the value of k_1 decreases. Since k_3, the rate of transfer with nonvertical excitation of *cis*-stilbene, depends on factors other than the spectroscopic excitation energy of the acceptor, $k_1/(k_2+k_3)$ may be small with low energy sensitizers.

The appearance of a new maximum at about 48 kcal per mole needs to be explained. The sudden increase in the value of $k_1(k_2+k_3)$ in this region cannot be easily reconciled with a 0-0 band for the *trans* triplet at about 50 kcal per mole. It is therefore suggested that because of Franck-Condon factors, the 0-0 band of *trans*-stilbene triplet has not been observed spectroscopically. The energy difference between successive vibrational levels in the *trans* triplet can be estimated from the vibrational structure of the $S_0 \rightarrow T_1$ absorption spectrum of *trans*-stilbene to be about 4 kcal per mole (11, 12). The lowest energy bands observed spectroscopically are at 49.5 (12) and 50.8 (11) kcal per mole. If these values represent the 0-1 absorption band, then a 0-0 band at 47±1 kcal per mole would fit in the observed vibronic progression within experimental uncertainty. The rationalization of the maximum at 48 kcal per mole in Figure 4 can now be based on the reasonable hypothesis that the rate of energy transfer from donor to acceptor first falls below the value for a diffusion controlled process when the excitation energy of the donor is less than the energy separation between the 0-vibrational level of the ground state and the 1-vibrational level of the triplet state in the acceptor. Experimental evidence in other acceptor-donor pairs supports this assertion, since it is generally found that the magnitude of rates of energy transfer first starts to drop when the process is still exothermic by 3 to 5 kcal per mole (50, 51). To complete the argument, it is required that the rate of energy transfer again approach the diffusion controlled magnitude when the 0-0 bands of acceptor and donor match perfectly in energy. It is perhaps highly significant that the above considerations, when applied to *cis*-stilbene as the energy acceptor, predict the minimum in Figure 5 at 57 kcal per mole. If the interpretation of the curve in Figure 5 is correct, it leads to the first example of the assignment of vibrational structure in spectroscopic states using photochemical means. Photochemists have realized for some time that spectroscopic data lead to information about excited states which is vital to the intimate understanding of the mechanisms of photochemical reactions. Notice is served to spectroscopists that the photochemical data presented here indicate that the reverse of this statement may also be true.

Levy and Szwarc (52) have noted that a good correlation exists between methyl affinities of aromatic hydrocarbons and their respective singlet-triplet excitation energies. They have pointed out that it may be possible to predict the triplet state excitation energy of aromatic molecules from their reactivity toward methyl radicals. It is very pleasing that the prediction of the singlet-triplet excitation energies of <u>cis</u>- and <u>trans</u>-stilbene using their respective methyl affinities is in precise agreement with the values predicted by the preceding analysis of Figure 5. Pertinent data are given in Table 24.

Table 24. Methyl Affinity Correlation with Triplet State Energy (52, 53)

	Methyl Affinity (85°)	E_T(kcal/mole)
Benzene	1	84.4
Biphenyl	5	65.4
Naphthalene	22	60.9
<u>cis</u>-Stilbene	47	(57)
Chrysene	58	56.6
Pyrene	125	48.5
<u>trans</u>-Stilbene	183	(47.7±1)
Benzanthracene	468	47.3
Anthracene	820	42.5

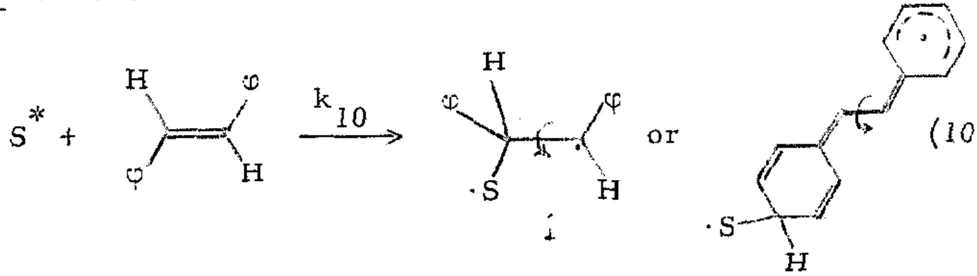
On the high energy side of Figure 5, where sensitizer energies can be accurately determined from their intense phosphorescence spectra in hydrocarbon glass at 77°K, the points fit the curve with remarkable precision. In fact, the curve should be useful in the estimation of energies for donors whose phosphorescence spectra have not been observed. In the course of this study, some apparent deviations from the curve have been found. Noted among these deviations were those of α- and β-naphthil. Careful study of the phosphorescence spectra of these two sensitizers revealed the presence of two stereoisomeric triplets in each case (54). Since the stereoisomeric triplets had different 0-0 band energies in their respective phosphorescence spectra, and since they were both capable of transferring energy to the stilbenes, the stationary states merely reflected the fact that effectively two sensitizers were being quenched by the stilbenes rather than one (as had been previously assumed). It is hoped that other deviations from the curve, when found, may initiate studies which, as in the case of the naphthils, will lead to a more intimate description of sensitizer triplet states.

The phosphorescence spectra of some of the sensitizers measured in EPA glass (diethyl ether, isopentane, ethanol; 5:5:2 by volume) show pronounced blue shifts relative to corresponding spectra in hydrocarbon glass (methylcyclohexane, isopentane; 5:1 by volume) (both at 77°K). For example, the 0-0 band of the phosphorescence spectrum of benzil is at about 61 kcal per mole in EPA and at 53.7 kcal per mole in hydrocarbon glass (54). The corresponding shift in 2,3-pentanedione is from 57.8 in EPA to 54.7 kcal per mole in hydrocarbon glass. Examination of Figure 5 indicates that if this solvent effect were to manifest itself in solution at room temperature, it would be reasonable to expect that the benzil and the 2,3-pentanedione sensitized stilbene isomerizations would lead to drastically different photostationary states in different solvents. Such a solvent effect was not observed experimentally. As is shown in Table 25, the stationary states vary only slightly in the three solvents used. The lack of significant variation in the photostationary states leads to a very important conclusion. It appears that to a first approximation only the acceptor-donor pair need be considered in describing the energy transfer process. This lends further support to the inference that triplet energy transfer occurs only when the acceptor and the donor are nearest neighbors in solution.

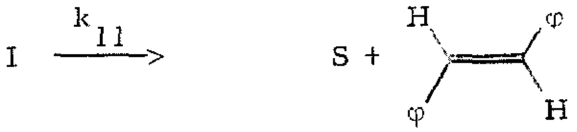
Table 25. Solvent Effect on the Sensitized Stilbene Isomerization.

Sensitizer	Solvent	T(°C)	% cis at P.S. State
2,3-Pentanedione	n-Heptane	28	91 ±1
	Benzene	28	87.5±1
	EPA	28	91 ±1
Benzil	n-Heptane	28	95 ±1
	Benzene	28	91 ±1
	EPA	28	93 ±1

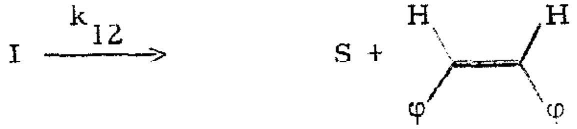
The fact that sensitizer concentration effects obey equation 9 (see Fig. 6) implies that transfer of energy to either stilbene produces an electronically excited species which can transfer energy to sensitizer molecules in their ground state. This point needs emphasis, since there is a school of thought which, especially in the case of sensitizers with lower energy, would prefer a mechanism for the sensitized isomerization involving the intermediary of an adduct diradical between sensitizer and either stilbene (55). This mechanism involves the reversible formation of a σ-bond between the sensitizer and the stilbene and does not include an electronically excited stilbene state in the scheme. It is shown in the equations below starting with trans-stilbene.



(10)

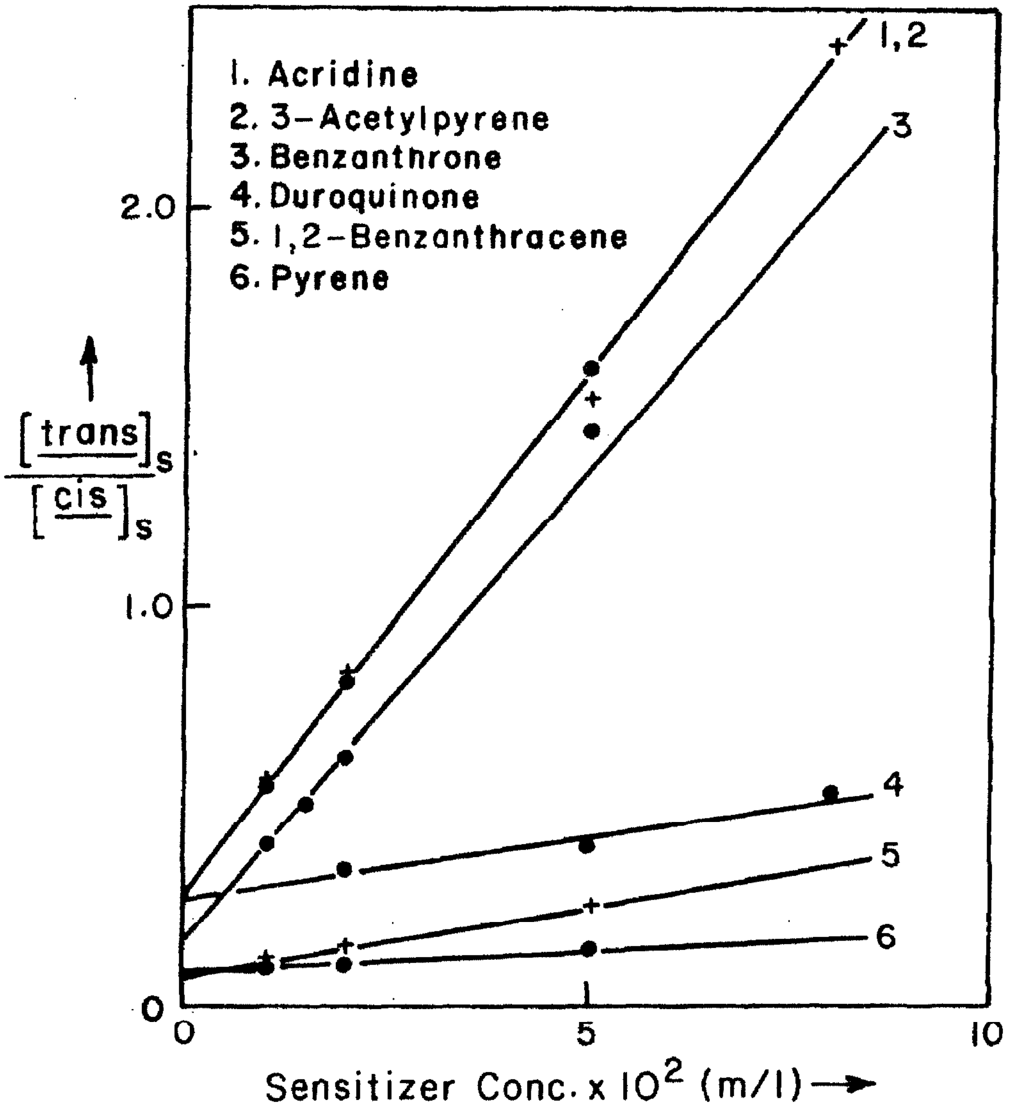


(11)



(12)

Fig. 6. Sensitizer Concentration Effect on Stilbene Isomerization.



Additional evidence in favor of the intermediacy of electronically excited stilbenes was provided by experiments in which azulene was included in the reaction mixtures. Since there is reason to believe that azulene has a very low energy triplet state, it was expected that its presence would be reflected in an alteration of the photostationary state composition of the stilbenes because it should be a very effective quencher of the *trans* triplets according to reaction 13.

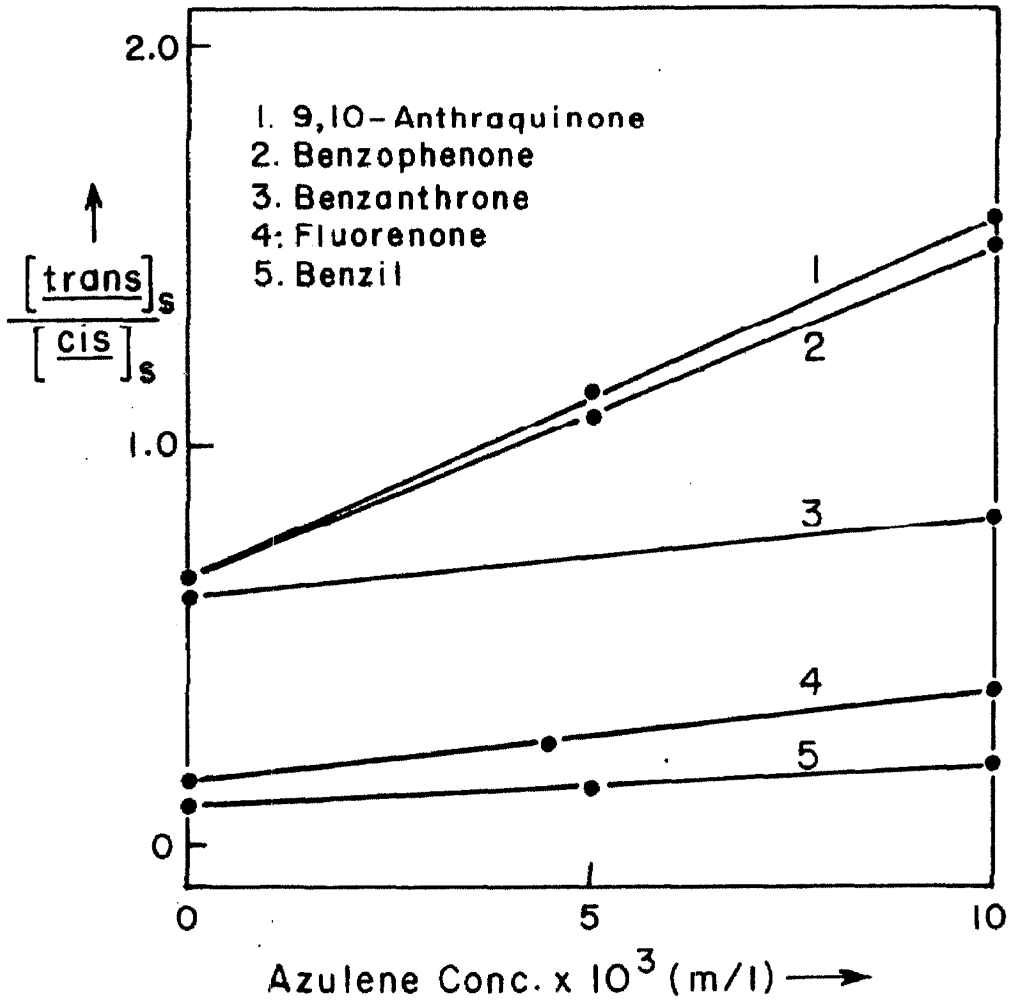
$$\underline{\text{trans}}^{*} + \text{Azulene} \longrightarrow \underline{\text{trans}} + \text{Azulene}^{*} \qquad (13)$$

Data for various azulene concentrations fitted the stationary state law 14, which includes equation 13 in the mechanism. As shown in

$$\frac{[\underline{\text{trans}}]_s}{[\underline{\text{cis}}]_s} = \frac{(k_2+k_3)(k_5+k_{-1}[S] + k_{13}[Az])}{k_1 k_6} \qquad (14)$$

Figure 7, the azulene effect was observed irrespective of the energy of the sensitizer. Clearly, at least in the cases shown in Figure 7, all energy transfer processes produce long-lived stilbene triplets which are quenched by azulene with the inevitable production of ground state *trans*-stilbene. This observation unequivocally demonstrates that reaction 3 does not deliver excitation to *cis*-stilbene as vibrational (thermal) energy. Except in the cases of eosin and 9,10-dibromoanthracene, an excellent argument against the exclusive operation of the adduct diradical mechanism in the remaining cases is the

Fig. 7. Azulene Concentration Effect on Stilbene Isomerization.



extreme sensitivity of the stationary states to the energy of the sensitizers. It should be pointed out that the above arguments do not apply against a mechanism in which the diradical can break up to give electronically excited states. In view of the fact that with almost all energy donors used in this work no adduct between the stilbenes and each donor could be detected, a diradical which would be an intermediate in equilibrium with excited states would merely be an unsatisfactory description of the energy transfer process.

The data in Figures 6 and 7 require further comment. Examination of equation 14 shows that the ratio of the slope to the intercept for the lines in Figure 6 should give k_{-1}/k_5 and that the same ratio for the lines in Figure 7 should give k_{13}/k_6, provided the condition $k_{-1}[S] << k_5$ holds. These ratios are shown in Tables 26 and 27, along with <u>maximum</u> (rather than average) experimental deviations. As required by the proposed mechanisms, the value of

Table 26. Extent of Reversibility in Energy Transfer with Various Sensitizers.

Sensitizer	E_T [a] (kcal/mole)	$k_{-1}/k_5 \times 10^{-2}$ (ℓ/mole)		
		Average	Maximum	Minimum
β-Acetonaphthone	59.3	0		
9-Fluorenone	53.0	0		
1,4-Duroquinone	51.7(?)	0.10	0.19	0.03
1,4-Benzoquinone	50.0(?)	0.37	0.51	0.25
Pyrene	48.5	0.14	0.18	0.08
1,2-Benzanthracene	47.3	0.52	?	0.52
Benzanthrone	46(?)	1.7	2.5	1.3
Acridine	45.3	0.87	1.05	0.80
3-Acetylpyrene	45.3(?)	0.88	1.12	0.74

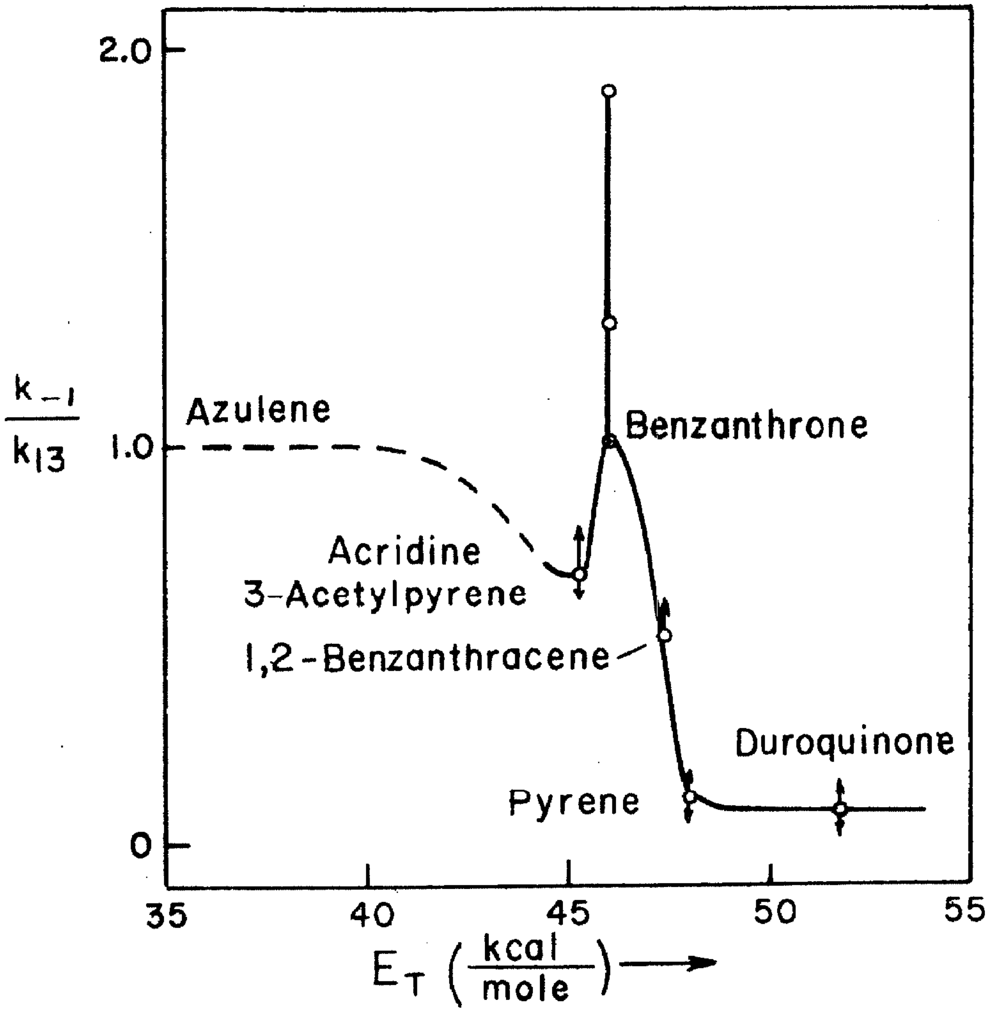
a. See appendix for references to triplet state energies.

Table 27. Relative Rate of Quenching of trans Triplet with Azulene.

Sensitizer	E_T (kcal/mole)	$k_{13}/k_5 \times 10^{-2}$ (ℓ/mole)		
		Average	Maximum	Minimum
Benzophenone	68.7	1.2	1.3	1.1
9, 10-Anthraquinone	62.4	1.4	1.6	1.2
Benzil	53.7	1.2	1.7	0.8
9-Fluorenone	53.0	1.4	1.6	1.3
Benzanthrone	46(?)	1.3	2.3	0.8

k_{13}/k_5 is independent of the energy of the sensitizer within experimental error. This indicates that azulene is seeing the same stilbene triplet(s) all along the curve in Figure 5. From Table 27, a best value for k_{13}/k_5 is 1.3×10^2. Since it has been shown that both benzophenone (50b) (E_T = 68.7) and anthracene (56) (E_T = 42) triplets are quenched by azulene at the diffusion controlled rate, it is very probable that k_{13} has the magnitude for a diffusion controlled process also. By dividing the values of k_{-1}/k_6 in Table 25 by 1.3×10^2, we obtain k_{-1}/k_{13}, which should be a measure of the deviation of k_{-1} from the diffusion controlled rate. In Figure 8, the values of k_{-1}/k_{13} are plotted against sensitizer energy. The point for 1,4-benzoquinone is not included in Figure 8 because in this case the result is complicated by the presence of ground state complexes between 1,4-benzoquinone and the stilbenes (see experimental). The arguments which were used to explain the appearance of the second maximum at 48 kcal per mole in Figure 5 lead to the prediction that Figure 8 should show a maximum when the sensitizer triplet state

Fig. 8. Relative Rates of Quenching of <u>trans</u> Triplet



energy matches the 0-0 band in the emission spectrum of the trans triplet. Such a maximum occurs at about 46 kcal per mole. That the maxima in Figures 5 and 8 should not coincide exactly in energy is not unexpected. The observation is in agreement with the fact that often the lowest energy transitions in absorption and emission spectra of molecules do not coincide when measured under identical conditions. In such cases, the lowest energy band in the absorption spectrum is found at higher frequency than the corresponding band in the emission spectrum (57). It appears that the trans triplet assumes a slightly different, less energetic, configuration between the time that it is produced and the time that it returns energy to an acceptor.

Since stilbene triplets transfer electronic excitation to either azulene or low energy sensitizers with the inevitable production of ground state trans-stilbene molecules, the intermediacy of a relatively long-lived triplet having a transoid configuration is demanded. The available data, however, do not exclude the possibility that some other triplet with non-cisoid configuration is involved. As was previously suggested (see introduction), the presence of such a triplet may account for the effect of temperature on the quantum yields of fluorescence and isomerization of trans-4-bromostilbene (12). The presence of this "phantom" triplet is also made reasonable by consideration of the apparent lifetime of the trans triplet. This quantity can be estimated from the results in Table 27. As has been pointed out, since energy transfer from anthracene triplets to azulene is diffusion controlled (56), it is likely that the more exothermic energy transfer from the trans-stilbene triplet to azulene is also diffusion controlled. Probably a good estimate for the magnitude of k_{13} is 10^{10} sec^{-1} ℓ $mole^{-1}$ (56). Since $k_{13}/k_5 = 130\ \ell\ /$ mole, it follows that $k_5 = 8 \times 10^7$ sec^{-1}. The apparent lifetime of the trans triplet, $(k_5 + k_6)^{-1}$, is thus less than 10^{-8} sec. This value is several orders of magnitude smaller than even the smallest experimentally determined lifetimes of other aromatic hydrocarbons (58). It indicates that the species observed by McCarty and MacLachlan (59) in double flash experiments of trans-stilbene in cyclohexane solution was incorrectly identified as the trans triplet . (This species had a mean lifetime of 40 m sec.) The absence of phosphorescence from olefins has been explained by Potts (60). This author pointed out that at least for compounds which are closely related to ethylene, Mulliken's calculations (24) indicate that the potential energy surfaces of the ground state and of the lowest triplet state intersect when the double bond is twisted by an angle of about 60°. Through this intersection, intersystem crossing into the ground state may be extremely rapid. If a perpendicular triplet is involved in the stilbene case, it must be in equilibrium with the trans triplet at room temperature and thus close to isoenergetic with it. Steps 15-17 would be included in the

$$t^* \rightleftharpoons p^* \qquad (15)$$

$$p^* \longrightarrow t \qquad (16)$$

$$p^* \longrightarrow c \qquad (17)$$

mechanism for stilbene isomerization. Inclusion of these steps leads to the prediction that the ratio of slope to intercept for the lines in Figure 7 is equal to $k_{13}/(k_5 + \frac{k_{15}}{k_{-15}} k_{16})$ rather than k_{13}/k_5. If the potential energy surfaces for the ground singlet state and the lowest triplet state of the stilbenes cross in the region of 90° of twist about the double bond, Potts' argument leads to the prediction that $k_{16} >> k_5$.

The potential function for twisting about the central bond in the lowest stilbene triplet state might look as is shown in Figure 9. The two possible nonvertical transitions of _cis_-stilbene are indicated by wavy arrows and the spectroscopic transitions by straight arrows.

The two triplets, if present, probably should each decay to either _trans_- or _cis_-stilbene with different efficiency (that is, $k_{16}/k_{17} \neq k_5/k_6$). Since different equilibrium compositions of _trans_ and "phantom" triplet should exist at different temperatures, a difference in decay ratios for the two triplets will be reflected in dependence of the photostationary states for different sensitizers on the temperature. As shown in Table 28, this expectation was realized experimentally. The [_cis_]/[_trans_] ratio at the stationary state

Fig. 9. Potential Function for Rotation in Stilbene Triplet States.

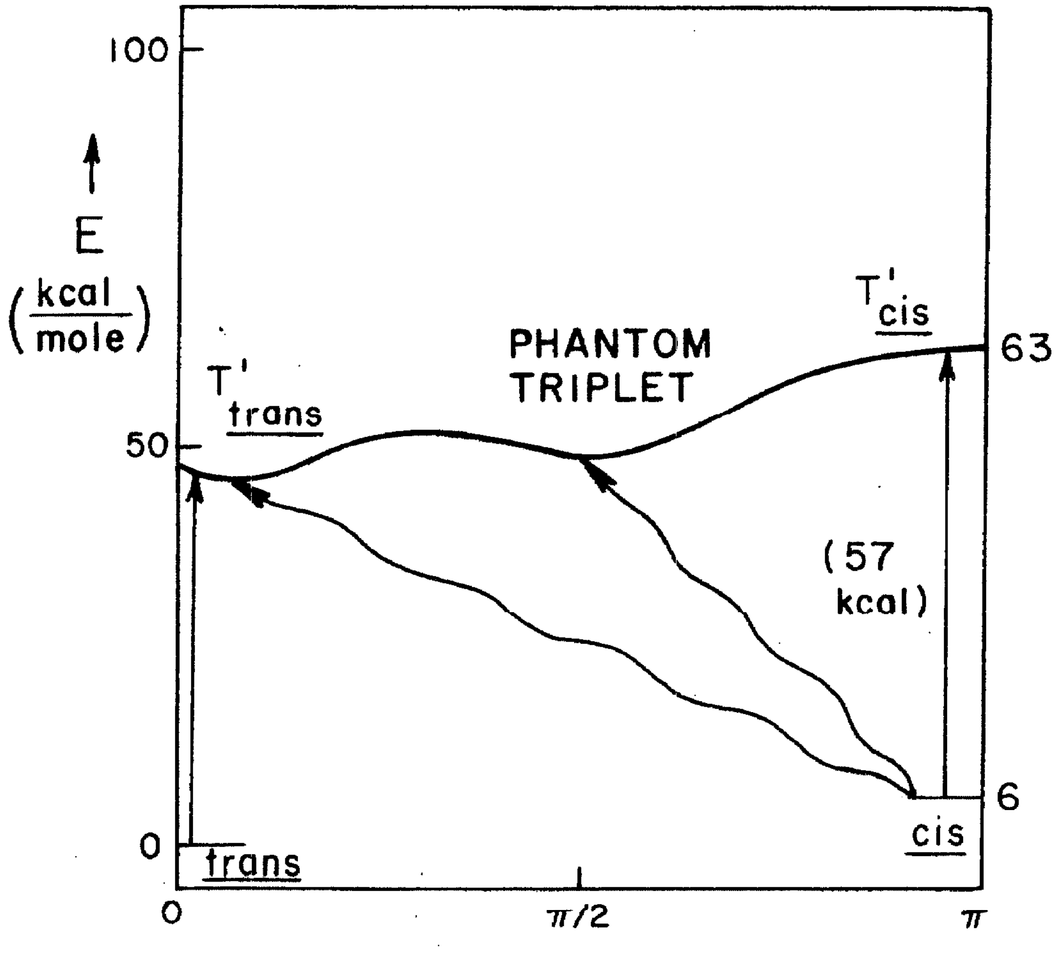


Table 28. Temperature Effect on Photostationary States.

Sensitizer	Temp. °C	$[C]_s/[t]_s$			$([C]_s/[t]_s)_{59}([C]_s/[t]_s)_{28}^{-1}$		
		Ave.	Max.	Min.	Ave.	Max.	Min.
Benzophenone	28	1.48	1.46	1.50	1.16	1.21	1.12
	59	1.72	1.68	1.76			
4-Acetylbiphenyl	28	1.85	1.89	1.81	1.18	1.26	1.12
	59	2.19	2.11	2.28			
2-Acetylfluorene	31	1.92	1.96	1.88	1.12	1.16	1.09
	59	2.16	2.19	2.14			
β-Naphthyl phenyl ketone	31	2.73	2.80	2.68	1.13	1.20	1.06
	59	3.10	3.22	2.98			
9-Fluorenone	28	6.25	6.42	6.09	1.39	1.50	1.30
	59	8.71	8.34	9.11			

increased by 12 to 40 per cent when the reaction temperature was raised by about 30°C. This effect can be accounted for by a mechanism involving the "phantom" triplet if it is assumed that the decay ratio of this triplet favors cis-stilbene more than the decay ratio of the trans triplet, and that the "phantom" triplet is slightly more energetic than the trans triplet. It should be emphasized that if the "phantom" triplet is included in the mechanism, reaction 6 is no longer demanded. Reaction 6 would be considered a possible process if upon isoenergetic intersystem crossing from the trans triplet, the excited ground state produced has a greater energy content than the transition state for the thermal isomerization of the stilbenes. Provided this condition is satisfied, then it is likely that the initially formed excited ground state will explore all ground state geometries in attempts to find suitable routes for radiationless deactivation.

Unfortunately, it is not possible to reach at this time any definite conclusions regarding the plausibility of reaction 6. As has been pointed out, a minimum energy for the trans triplet is 46 kal per mole. This value is bracketed by the two available independent measurements of the transition state energy for the thermal isomerization of the stilbenes, 48 (21) and 43 (20) kcal per mole, respectively.

That the observed temperature effect must be reflected in the decay process rather than in the excitation step is fairly certain. For all the sensitizers in Table 28, energy transfer to trans-stilbene is exothermic, and, except in the case of fluorenone, it should be diffusion controlled. Except for benzophenone, energy transfer from the sensitizers to the cis-isomer has become relatively inefficient as reflected by photostationary states which are richer in cis-stilbene. Thus, if significant activation energies were involved in the excitation steps, they should be greater for the excitation of the cis-isomer. This predicts that at higher temperatures the stationary states should become richer in trans-stilbene. This is contrary to the results in Table 28. The result for fluorenone is especially significant. This sensitizer does not possess the energy necessary to excite cis-stilbene to the spectroscopic cis triplet. In this case, if reaction 2 were important, the excitation of cis-stilbene should have a significant activation energy. Such an activation energy is not reflected in the measurements made, a fact which lends further support to the involvement of nonvertical excitation of cis-stilbene to either the trans or the "phantom" triplet. Actually, it appears that with fluorenone, raising the temperature increases the cis content of the stationary mixture to a greater extent than would be expected from the temperature effect attributed to the decay process. The fact that the point for fluorenone is below the first maximum in Figure 5 indicates that the rate of energy transfer to trans-stilbene, k_1, is less than diffusion controlled for this sensitizer. If the activation energy for the nonvertical excitation of cis-stilbene is smaller than the activation energy for the excitation of trans-stilbene, fluorenone will behave at the higher temperature more like a high energy sensitizer (say benzil). The results in Table 28 indicate this to be the case.

Two other mechanisms which might explain the effect of temperature without the involvement of a "phantom" triplet should also be mentioned. The first is merely the mechanism given by equations 1 to 6. Within the framework of this mechanism, one can account for the temperature effect if it is assumed that the decay of the trans triplet, steps 5 and 6, is activated. It can be easily shown that if the activation energy for step 6 is greater by 1 kcal per mole than that for step 5, the [cis]/[trans] ratio at the stationary state will increase by 15 per cent on raising the temperature from 28 to 59°C. The second mechanism involves the assumption that the activated process is in the interaction of ground state stilbene molecules with the *trans* triplet in steps such as shown in equations 18 and 19. Such

$$\underline{\text{trans}}^{*} + \underline{\text{trans}} \rightleftharpoons \text{excimer}^{*} \tag{18}$$

$$\text{excimer}^{*} \longrightarrow 2\ \underline{\text{trans}} \tag{19}$$

a mechanism has been proposed (5) as an explanation for temperature effects (2) observed in the unsensitized photoisomerization of the stilbenes. That the overall process described in steps 18 and 19 occurs in the sensitized isomerization has been established. The evidence will be discussed later. Use of this scheme to explain the results in Table 28 is made particularly attractive because it has been reported that the benzophenone sensitized isomerization of the stilbenes using very dilute solutions (in which decay of the *trans* triplet by interaction with ground state molecules should be negligible) is not temperature dependent (29b). However, the stationary state at infinite dilution of stilbene in the presence of benzophenone is $[\text{cis}]_s/[\text{trans}]_s = 1.60$ (61). The maximum temperature effect that can be accommodated by the mechanism which assumes (as a first approximation) that only steps 18 and 19 are temperature dependent cannot lead to stationary ratios greater than 1.60 for the benzophenone sensitized isomerization. At best, at the higher temperature the equilibrium in step 18 will overwhelmingly favor the left side and the same stationary state as is obtained at infinite dilution would result. Since the observed ratio for the benzophenone sensitized isomerization at the higher temperature is at least 5 per cent greater than this limit, steps 18 and 19 cannot be the only activated processes involved. The data presented here predict that the stationary state for the sensitized isomerizations will be temperature dependent even at infinite dilution. Reports to the contrary are puzzling and should be checked.

If the mechanism for the sensitized isomerization of the stilbenes were given by equations 1 to 6 and interactions of triplet states with ground state molecules, such as shown in equations 18, 19, and the reverse of reaction 1 were not important, then a study of the trans to cis and the cis to trans quantum yields for the stilbenes should provide a quantitative measure of the quantum yields of intersystem crossing for the various sensitizers. As is shown by equations 20 and 21, the sum of the quantum yields equals f, the sensitizer inter-

$$\frac{1}{Q_{t\to c}} = \frac{k_5+k_6}{f\,k_6}\left(1 + \frac{k_{22}}{k_1[\underline{\text{trans}}]}\right) \tag{20}$$

$$\frac{1}{Q_{c\to t}} = \frac{k_5+k_6}{f\,k_5}\left(1 + \frac{k_{22}}{(k_2+k_3)[\underline{\text{cis}}]}\right) \tag{21}$$

system crossing yield, provided no quenching process of sensitizer triplets, equation 22, is competing with quenching by either cis or

$$S^* \longrightarrow S + E \tag{22}$$

trans stilbene (i.e., $k_1[\textit{trans}]$ and $(k_2+k_3)[\textit{cis}] \gg k_{22}$).

Furthermore, if the above conditions are satisfied, the ratio of the quantum yields should predict the photostationary state for high energy sensitizers (i.e., it should depend only on the rate constants for decay of the stilbene triplets).

Preliminary quantum yields were measured in this work. These were checked and extended by Dr. D. Cowan (61). Selected results for the benzophenone sensitized isomerization are shown in Table 29.

Table 29. Quantum Yields for the Benzophenone Sensitized Isomerization of *trans*- and *cis*-Stilbene in Benzene.

Benzophenone conc. in m/ℓ	Stilbene conc. in m/ℓ	$Q^{a,c}_{t\to c}$	$Q^{b}_{t\to c}$	$Q^{a,c}_{c\to t}$
0.100	0.050	0.41		
0.050	0.100			0.35
	0.050	0.44	0.41	0.38
	0.030		0.41	
	0.025	0.44		
	0.010		0.44	
	0.005		0.45	
	0.001	0.47	0.48	0.37

a. Results by Dr. D. Cowan.
b. This work.
c. Benzophenone used in these runs was zone refined.

The experimental uncertainty in individual entries in Table 29 varied between 2 and 5 per cent. The reproducibility of independent experiments was also in the range of 2-5 per cent. Dr. D. Cowan's values are in general the more reliable of the two sets, but the agreement between his values and those from this work is satisfactory.

Examination of Table 28 shows that the ratio of the quantum yields does not predict the photostationary state. Furthermore, it appears that whereas the *cis*→*trans* quantum yield is independent of the concentration of stilbene, the *trans*→*cis* quantum yield increases as the concentration of stilbene is decreased. Clearly, some interaction between ground state *trans*-stilbene molecules and *trans* triplet must serve to decrease the rate of isomerization at the higher stilbene concentrations. This concentration effect, if real, should also be reflected in the photostationary states. It was found that with 0.05 M benzophenone, the [*cis*]/[*trans*] ratio at the stationary state increased from 1.43 to 1.59 (61) when the stilbene concentration was 0.05 M and 0.001 M, respectively. This is in agreement with the ratio of 1.6 reported for very dilute stilbene solutions ($\sim 10^{-4}$M) (29b). The effect found, however, is smaller than expected if *trans*-stilbene ground state were the only quenching agent. Apparently, sensitizer ground states are also effective in quenching the *trans* triplet to ground state *trans*-stilbene. Experimentally, this is verified, since it was found that in general *trans*→*cis* quantum yields determined in the presence of higher concentrations of sensitizers are lower (*vide infra* and Table 29).

If equations 23 and 24 are included in the mechanism, the following

$$\underline{\text{trans}}^{*} + \underline{\text{trans}} \longrightarrow \text{excimer}^{*} \longrightarrow 2\ \underline{\text{trans}} \tag{23}$$

$$\underline{\text{trans}}^{*} + \text{S} \longrightarrow (\text{S}\cdots\underline{\text{trans}})^{*} \longrightarrow \underline{\text{trans}} + \text{S} \tag{24}$$

relationships may be derived for sensitizers with triplet state energies greater than 62 kcal per mole (i.e., such that $k_1 = 0$, $k_{22} << k_1[t]$ or $k_2[c]$ and $k_1 = k_2$).

$$\frac{1}{Q_{t\to c}} = \frac{1}{f(k_6 - k_{24}[S])} \left(k_5 + k_6 + k_{23}[t] + k_{24}[S]\right) \tag{25}$$

$$\frac{1}{Q_{c\to t}} = \frac{k_5 + k_6}{f\,k_5} \tag{26}$$

$$\frac{[c]_s}{[t]_s} = \frac{1}{k_5(k_5+k_6+k_{24}[S])} \left[k_6(k_5+k_6 - \frac{k_{23}[c]_s\left\{(k_5+k_6)^2 - k_5 k_{24}[S]\right\}}{(k_5+k_6+k_{24}[S])} \right] \tag{27}$$

In the absence of quenching steps, 23 and 24, the stationary state is $[\underline{\text{cis}}]_s/[\underline{\text{trans}}]_s = k_6/k_5 = 1.60$. It follows that the maximum trans→cis quantum yield should be given by equation 28. This quantum

$$Q_{t\to c} = 1.60\,Q_{c\to t} = 0.58_7 \tag{28}$$

yield should be attained as the concentrations of sensitizer and trans-stilbene approach zero. The trans→cis quantum yield for $[S] = 0.05$ M and $[t] = 0.001$ M should reflect only effects of the concentration of the sensitizer. Using the observed value (0.48) and equation 25, and assuming that $k_{24} >> 0.02\,k_{23}$, we get equation 29. From

$$\frac{1}{0.48} = \frac{1}{f(k_6 - .05\,k_{24})} \left(k_5 + k_6 + .05\,k_{24}\right) \tag{29}$$

equations 29, 30, and 31, we can calculate $k_{24}/k_6 = 2.4\ M^{-1}$.

$$f = 2.60\ Q_{c \rightarrow t} = 0.95 \tag{30}$$

$$k_6 = 1.60\ k_5 \tag{31}$$

Using equation 27 and the dependence of the $[\underline{\text{cis}}]_s/[\underline{\text{trans}}]_s$ ratio on the concentration of stilbene, the ratio $k_{23}/k_6 = 2.3\ M^{-1}$ can be obtained.

An independent check of the values of k_{24}/k_6 and k_{23}/k_6 can now be made. Equation 27 can be used to calculate the trans→cis quantum yield for 0.050 M benzophenone and 0.050 M trans-stilbene. The calculated value, 0.45, agrees well with the experimental 0.44. Although these results are promising and present strong evidence in favor of processes such as are shown in equations 23 and 24, more work should be done to document these phenomena more precisely. The ratios of k_{23}/k_6 and k_{21}/k_6 do not satisfactorily predict the trans→cis quantum yield for 0.10 M benzophenone and 0.050 M trans-stilbene (calculated value using equation 25 is 0.37, observed is 0.41), and it is possible that a more detailed study in this area will either remove the discrepancy or lead to a better theory for the explanation of the results.

Equations 23 and 24 were neglected in the treatment of the data in Figures 5, 6, 7, and 8. This simplification is justified since it was shown that their inclusion in the mechanism does not in any way affect the conclusions reached. The values for the ratios of rate constants shown in Tables 26 and 27 are not affected to a degree greater than the indicated experimental uncertainty.

It should be pointed out that if the results of Fischer and Malkin are taken at face value, one is forced to the conclusion that reaction 24 cannot be important. This follows from their contention that the stationary state for the benzophenone sensitized stilbene isomerization is independent of the concentration of benzophenone. A discrepancy between Fischer's results and those presented here has already been pointed out in the discussion on temperature effects. Until at least that discrepancy is removed, it is felt that other of Fischer's results may also be considered questionable.

The possibility that the concentration effects observed are due to the introduction of quenchers which are present in trans-stilbene and benzophenone as impurities is not likely. The results indicate that $\frac{k_{13}}{k_{23}} \approx \frac{k_{13}}{k_{24}} = 50$. To obtain the minimum quencher concentration that will accommodate the results, it is assumed that this quencher is as effective an acceptor of energy from trans triplets as azulene (probably by a diffusion controlled process). Then if, for example in the case of benzophenone, a proportionality is assumed between quencher concentration, $[Q]$, and sensitizer concentration, $[S]$, we can calculate the fraction of quencher as shown in equations 32 to 36. Two per cent impurity content in either the benzophenone or the trans-stilbene used for the experiments in question is not

$$[Q] = \alpha[S] \tag{32}$$

$$k_{21} = k_q\alpha = k_{13}\alpha \tag{33}$$

$$\frac{k_{13}}{k_{21}} = 50 \tag{34}$$

$$\frac{k_{13}}{k_{13}\alpha} = 50 \tag{35}$$

$$\alpha = 0.02 \tag{36}$$

acceptable (see experimental for purification of these compounds). It should be pointed out that even if impurities were present it would be improbable that they would possess triplet states lower than 50 kcal per mole, and thus would not be expected to be effective quenchers of the trans triplet.

A possible quenching process which cannot be ruled out at this time may involve a transient photoproduct of the sensitizer. For example, in the case of benzophenone, such a product may be dihydrofluorenone (see (62) for analogous reactions).

Steps such as shown in equation 23 have been reported as being of importance in the decay of chlorophyll triplets (63). However, in this case the possibility of quenching by impurities in the chlorophyll could not be ruled out.

The approximate expressions 20 and 21 indicate that for sensitizers with short lifetimes, it should be possible to observe a decrease in the quantum yields for isomerization as the concentration of stilbene is decreased. Provided k_{22} is large, the condition $k_{22} \geq k_1$[trans] might hold for stilbene concentrations sufficiently large to permit the experimental determination of quantum yields ([trans] ≥ 0.001 M.) The trans→cis quantum yields for fluorenone (Table 30) are in accord with this prediction. Interestingly, the values for the quantum yields appear to decrease at the two concentration limits. Presumably, at the highest concentration quenching of trans triplet by ground state trans-stilbene is occurring, whereas at the lowest stilbene concentrations radiationless decay of the fluorenone triplets competes with energy transfer to trans-stilbene.

Table 30. trans→cis Quantum Yields for the Fluorenone Sensitized Stilbene Isomerization in Benzene.

9-Fluorenone conc. in m/ℓ	Stilbene conc. in m/ℓ	$Q_{t\rightarrow c}$	$Q_{c\rightarrow t}$
0.100	0.050	0.41[a]	0.23[a]
0.050	0.100	0.41	0.25
	0.050	0.44	
	0.040	0.42	
	0.030	0.43	0.21
	0.020	0.39	
	0.010	0.33	0.20
	0.005	0.40	
	0.001	0.28	

a. This measurement by Dr. D. Cowan (61).

It was initially hoped that use of equation 20 and data such as shown in Table 30 would permit the evaluation of relative radiationless decay rates (k_{22}) for various sensitizers. Unfortunately, complications involving quenching of the trans triplet by ground state molecules make trans-stilbene a poor candidate for studies of this type. Since the cis→ trans quantum yield is apparently not sensitive to processes such as shown in equations 23 and 24, equation 21 is probably exact and should be subjected to experimental test.

A very important result of the study of cis→ trans quantum yields was given by equation 30. The calculated intersystem crossing quantum yield for benzophenone is 0.95.

This value checks exactly with that predicted by the quantum yields of the benzophenone sensitized isomerization of cis- and trans-1,2-diphenylpropene (64), and is not much different from unity, the value estimated from independent studies (65).

As shown in Table 31, the quantum yields of stilbene isomerization for several other ketones are sufficiently similar to those found

Table 31. Quantum Yields of Sensitized Stilbene Isomerization in Benzene.[a]

Sensitizer	Conc. m/ℓ	Stilbene conc. m/ℓ	$Q_{t \rightarrow c}$	$Q_{c \rightarrow t}$
Benzophenone	0.05	0.05	0.44	0.37
Acetophenone	1.0	0.05	0.40	0.37
Fluorenone	0.05	0.10	0.41	0.23
Michler's ketone	0.10	0.05	0.42	---
4-Methylbenzophenone	0.05	0.05	0.42	---

a. Values determined by Dr. D. Cowan (61).

for benzophenone to suggest that they all intersystem cross with high efficiency. Approximate quantum yields for three more ketones, benzil, flavone, and β-naphthyl phenyl ketone, are also in the range of 0.3 to 0.5 for both processes.

The quantum yield measurements provide an additional convincing argument against the possibility that the nonvertical excitation of cis-stilbene merely involves transfer of vibrational energy. Since the trans→cis quantum yields for fluorenone (Table 30) for high stilbene concentrations are practically identical with those found for benzophenone, it is expected that the maximum cis→trans quantum yield for fluorenone will be 0.37. The quantum yield for 0.01 M cis-stilbene in benzene is 0.20. This value makes it possible to calculate that cis-stilbene is more active than benzene as an energy acceptor by at least a factor of 1000. This estimate of relative reactivities is based upon the hypothesis that radiationless deactivation of fluorenone triplets is due entirely to transfer of vibrational energy to individual benzene molecules. It probably vastly underestimates the special role of cis-stilbene as acceptor of energy (66).

The possibility that the information which has resulted from this study can lead to a better understanding of the mechanism of the unsensitized stilbene isomerization will be examined now. Several discussions of this mechanism have appeared in the literature recently, and the spectroscopic and photochemical data have received various interpretations (see introduction). One point about which there seems to be universal agreement is that the isomerization does not occur in the first excited singlet states. By default, therefore, triplet states have been usually proposed as the intermediates. In this study, the behavior of the stilbene triplets was studied and the fact that isomerization can occur by way of the lowest triplet states seems to have been unequivocally confirmed. Although absolute proof for the involvement of triplet states for the isomerization under conditions of direct irradiation is still lacking, several considerations make this hypothesis very attractive.

The "natural" decay ratio of stilbene triplets has been shown to be [cis]/[trans] = 1.60. If it is assumed that the quantum yield for intersystem crossing is unity for both stilbene isomers, then the stationary state for irradiation with monochromatic light of wavelength λ should be given by equation 37,

$$\frac{[\underline{\text{cis}}]_s}{[\underline{\text{trans}}]_s} = 1.60 \left(\frac{\epsilon_t}{\epsilon_c} \right)_\lambda \qquad (37)$$

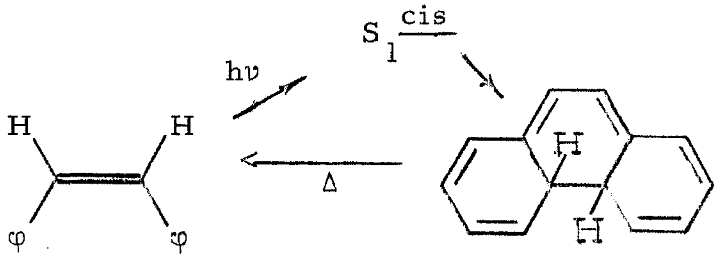
where ϵ_t and ϵ_c are the extinction coefficients of trans- and cis-stilbene, respectively, at the wavelength in question. Observed and calculated stationary states for irradiation with the 3130 Å mercury line are shown in Table 32. The agreement between calculated and observed values is excellent. It should be pointed out that the concentrations used for the measurements in Table 32 are sufficiently

Table 32. Photostationary States for the Stilbenes (3130 Å).

Stilbene conc. m/ℓ	Solvent	ϵ_t/ϵ_c at 3130 Å	% cis at Stationary State obs.	calc.	Ref.
$1x10^{-5}$	n-Hexane		93.0		10
$4x10^{-5}$	Isohexane		93.0		18
	Isoöctane	7.2		92.0	7
$1.6x10^{-3}$	Benzene	5.83	89.7	90.3	This work

low to render contribution by process 20 to the stationary state negligible.

A unique feature of the unsensitized isomerization is the formation of an orange transient from cis-stilbene. This transient has been shown to react with oxygen with the subsequent formation of phenanthrene (3) and to revert thermally to cis-stilbene in the absence of light. It has been postulated that it is the dihydrophenanthrene (DHP) shown in equation 38.



(38)

Confirmatory evidence for the formation of this species was obtained independently in this study (see experimental). At 30°C the decay of the species was first order and its mean lifetime was calculated to be 185 min. Assuming a minimum extinction coefficient (10^3) for its absorption maximum (4550 Å), its maximum photostationary state concentration achieved upon irradiation with 3130 Å light of either cis- or trans-stilbene (0.050 M in benzene) was estimated to be 8 x 10^{-4} M. It is very likely that the transient has a lower triplet state energy than the trans triplet. If so, it should affect the [cis]/[trans] ratio of stilbenes at the stationary state by serving as an electronic energy acceptor. Reactions 39, 40, and 41

$$\underline{\text{trans}}^{*} + \text{DHP} \longrightarrow \underline{\text{trans}} + \text{DHP}^{*} \tag{39}$$

$$\text{DHP}^{*} \longrightarrow \underline{\text{cis}} \tag{40}$$

$$\text{DHP}^{*} \longrightarrow \underline{\text{trans}}^{*} \tag{41}$$

are likely. Their consequence would be to increase the [trans]/[cis] ratio at the stationary state (essentially the azulene effect) and to keep the steady state concentration of transient low. Clearly, the interference of the dihydrophenanthrene intermediate should be maximized by increasing the total stilbene concentration and lowering the reaction temperature. Since, despite its long lifetime in the dark, the steady state concentration of transient is very small, there must exist photochemical paths for its destruction. Steps 39 and 40 should become important when its concentration approaches and exceeds 10^{-3} M. Provided the triplet state of the transient is lower than that of the trans triplet, such a concentration effect is demanded by the results with azulene. That the transient is not formed by way of stilbene triplets was conclusively shown, since its absorption spectrum was not observed in experiments with sensitizers. For this reason, equation 41 is considered a very likely path for the fate of triplet dihydrophenanthrene. The possibility that equation 42, followed by

$$S^{*} + DHP \longrightarrow S + DHP^{*} \qquad (42)$$

equation 41, is responsible for the failure to detect the transient in the sensitized experiments is not tenable. Equation 39 could be at best diffusion controlled. Since most of the sensitizer triplets would still be quenched by stilbene ground state molecules, equation 42 could not become important in the absence of a detectable amount of dihydrophenanthrene. The possibility of destruction of the transient by means of singlet energy transfer from the sensitizer, although real, is probably not a sufficient reason for the failure to detect it in the presence of sensitizers. Singlet energy transfer from trans-stilbene should also be possible in the unsensitized irradiation, and yet transient formation under the latter conditions is detected.

Thus, assuming a triplet mechanism, the results presented here lead to the expectation that the stationary states for the unsensitized isomerization of the stilbenes should be dependent upon the stilbene concentration for two reasons. At concentrations greater than 10^{-3} M, ground state interaction with the trans triplet, equation 23, should become important and, very likely, at stilbene concentrations greater than 0.05 M, equation 39 should come into play. Both effects lead to the prediction that at higher stilbene concentrations the [trans]/[cis] ratio at the stationary state should be higher.

Although such a concentration effect was observed in this work (see experimental), the effect was much better documented by D. Schulte-Frohlinde et al. in the case of 4-nitro-3'-methoxystilbene (5). Their results are shown, in part, in Table 33. If it is assumed that in this concentration range the important factor which leads to the observed concentration effect is equation 23, then the mechanism for the unsensitized photoisomerization of 4-nitro-3'-methoxystilbene can be summarized by the following equations:

Table 33. Quantum Yields and Stationary States for the Isomerization of 4-Nitro-3'-methoxystilbene in 1-Methylnaphthalene with 3660 Å Light.

Concentration m/ℓ	$Q_{t \to c}$	Equilibrium % cis
1.0×10^{-4}	0.31	81.0
5.0×10^{-4}	0.30	77.5
5.0×10^{-3}	0.29	77.5
1.0×10^{-2}	0.25	75.5
5.0×10^{-2}	0.22	58.5
1.0×10^{-1}	0.18	41.0

$$\underline{\text{trans}} \xrightarrow{h\nu} \underline{\text{trans}}^{**} \qquad (43)$$

$$\underline{\text{cis}} \xrightarrow{h\nu} \underline{\text{cis}}^{**} \qquad (44)$$

$$\underline{\text{trans}}^{**} \longrightarrow \underline{\text{trans}} \qquad (45)$$

$$\underline{\text{trans}}^{**} \longrightarrow \underline{\text{trans}}^{*} \qquad (46)$$

$$\underline{\text{cis}}^{**} \longrightarrow \underline{\text{cis}} \qquad (47)$$

$$\underline{\text{cis}}^{**} \longrightarrow \underline{\text{cis}}^{*} \qquad (48)$$

$$\underline{\text{cis}}^{*} \longrightarrow \underline{\text{trans}}^{*} \qquad (4)$$

$$\underline{\text{trans}}^{*} \longrightarrow \underline{\text{trans}} \qquad (5)$$

$$\underline{\text{trans}}^{*} \longrightarrow \underline{\text{cis}} \qquad (6)$$

$$\underline{\text{trans}}^{*} + \underline{\text{trans}} \longrightarrow \text{excimer}^{*} \longrightarrow 2\ \underline{\text{trans}} \qquad (23)$$

In the above mechanism, double stars denote excited singlet states and single stars denote triplet states.

Using the above mechanism, equations 49 and 50, which predict

$$\frac{1}{Q_{t\to c}} = \frac{k_{45} + k_{46}}{k_{46}} \left(\frac{k_5 + k_6}{k_6} + \frac{k_{23}}{k_6} [\underline{\text{trans}}] \right) \qquad (49)$$

$$\frac{[\text{trans}]_s}{[\text{cis}]_s} = \frac{\varepsilon_c\ k_{48} (k_{45} + k_{46})}{\varepsilon_t\ k_{46} k_6 (k_{47} + k_{48})} (k_5 + k_{20} [\underline{\text{trans}}]_s) \qquad (50)$$

the expected concentration dependences , can be derived. The possibility that excited singlet states are interacting with ground states has been neglected from the mechanism.

The fit of the data in Table 33 to equations 49 and 50 is shown by Figures 10 and 11, respectively. Since the values in Table 32 are subject to 10 per cent experimental uncertainty, the deviations of the points from the lines in Figures 10 and 11 are well within the error limits. Despite the satisfactory fit obtained, these results are not entirely pleasing. Using the intercepts and slopes in Figures

Fig. 10. trans→ cis Quantum Yields for 4-Nitro-3'-methoxystilbene as a Function of Stilbene Concentration.

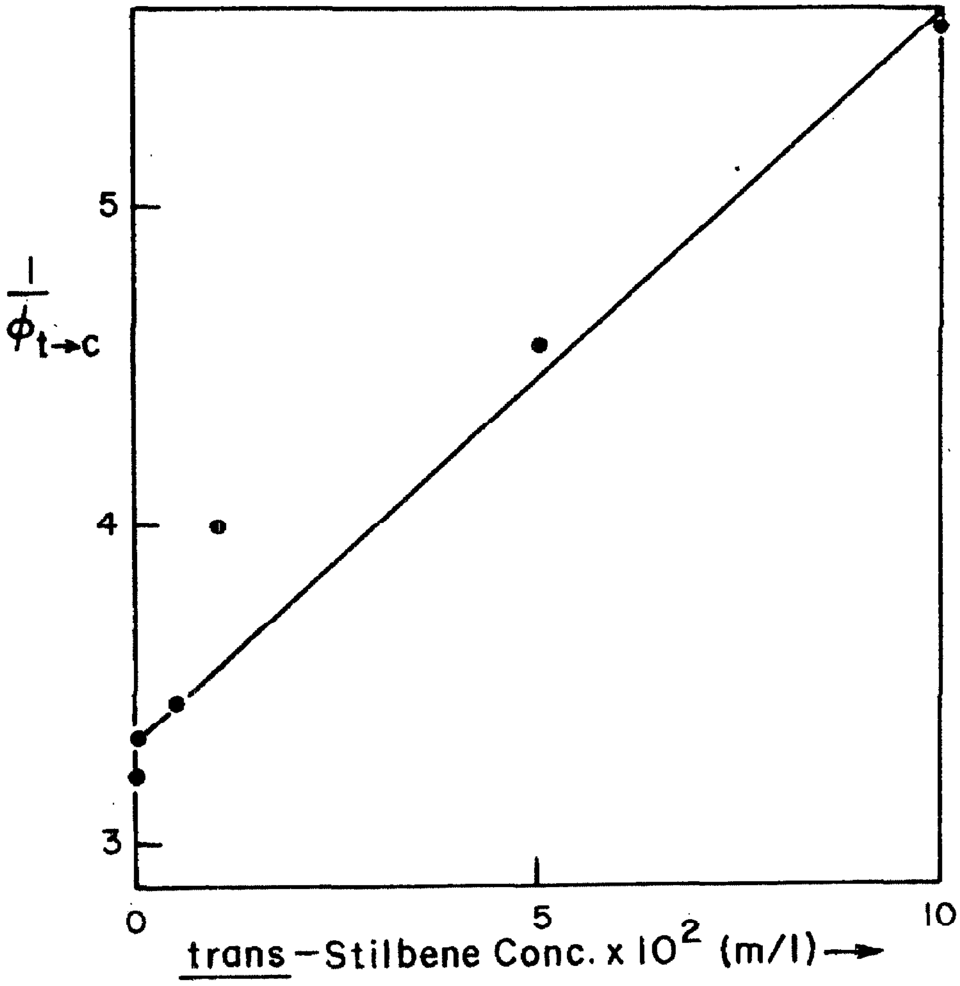
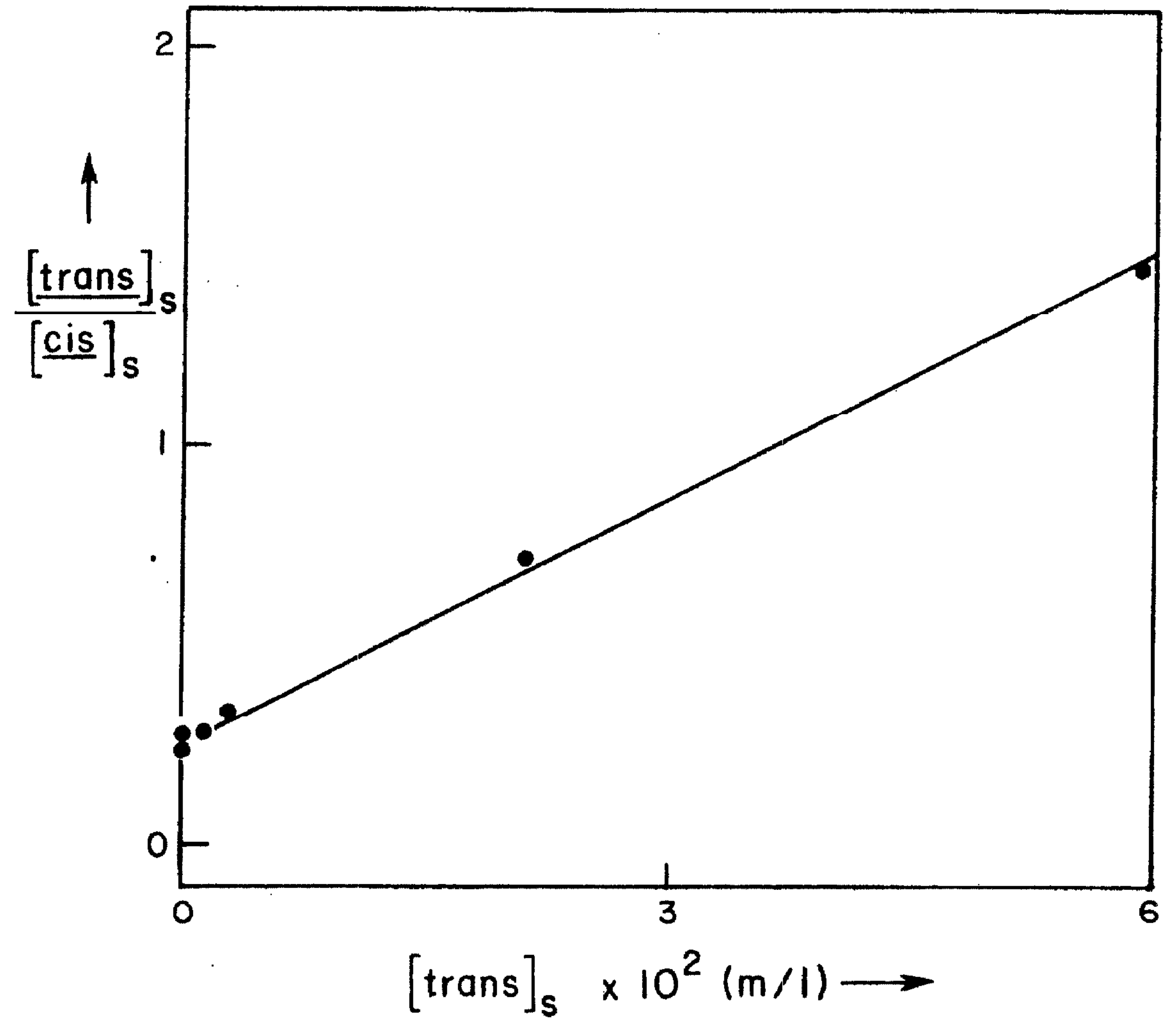


Fig. 11. Stationary State Dependence on 4-Nitro-3'-methoxystilbene Concentration in 1-Methylnaphthalene.



10 and 11 and equations 49 and 50, the following ratios of rate constants can be calculated:

$$\frac{k_{20}}{k_5+k_6} = 7.2 \tag{51}$$

$$\frac{k_{20}}{k_5} = 78 \tag{52}$$

$$k_6 = 9.8\,k_5 \tag{53}$$

$$\frac{k_{43}}{k_{43}+k_{42}} = 0.33 \tag{54}$$

$$\frac{k_{45}}{k_{44}+k_{45}} = 0.85\,\frac{\epsilon_t}{\epsilon_c} \tag{55}$$

Although the values calculated, equations 51 to 55, are consistent with the available data for the isomerization of 4-nitro-3'-methoxystilbene in 1-methylnaphthalene, two serious objections should be pointed out. The cis→trans quantum yield has been shown to be independent of the solvent used, the average value for several solvents (this quantity appears not to have been measured in 1-methylnaphthalene) being 0.4. The calculated value of $\frac{k_6}{k_5}$, equation 53, demands that the maximum cis→trans quantum yield in 1-methylnaphthalene be 0.1. It is not likely that the triplet decay ratio should be so altered exclusively by 1-methylnaphthalene. Finally, the intersystem crossing ratio for excited cis singlets, equation 55, cannot be larger than unity, however, the ratio of the extinction coefficients of the two isomers at 3660 Å in 1-methylnaphthalene, if known, would probably predict a higher value.

To detect the presence of trans triplets in the unsensitized stilbene isomerization, the stilbenes were irradiated with 3130 Å light in benzene solutions containing azulene. It was found that, as in the case of the sensitized isomerization, the presence of azulene led to photostationary states which were richer in trans-stilbene. Although the observed effect suggests that equation 13 is involved and that trans triplets are intermediates in the unsensitized isomerization of stilbene, the results fell short of expectation. The stationary states for different azulene concentrations are shown in Table 34. If the only way in which the presence of azulene affects the

Table 34. Effect of Quenchers on the Unsensitized Stilbene Isomerization (3130 Å light).

Quencher	Conc. of Quencher (m/ℓ)	Total Stilbene Conc. (m/ℓ)	% cis at the Stationary State
None	----	1.60×10^{-3}	89.5
Azulene	4.0×10^{-3}		88.4
	8.0×10^{-3}		87.5
	12.0×10^{-3}		87.0
	20.0×10^{-3}		85.5
$Fe(DBM)_3$	1.6×10^{-3}		89.8
	2.4×10^{-3}		89.4

stationary state were by intercepting trans triplets, equation 13, then the [trans]/[cis] ratio at the photostationary state should depend linearly upon the azulene concentration. As shown in Figure 12, this is not the case. Furthermore, the value of $k_{13}/k_5 = 30$ calculated from the initial slope of the curve in Figure 12 is not as large as found previously (Table 27).

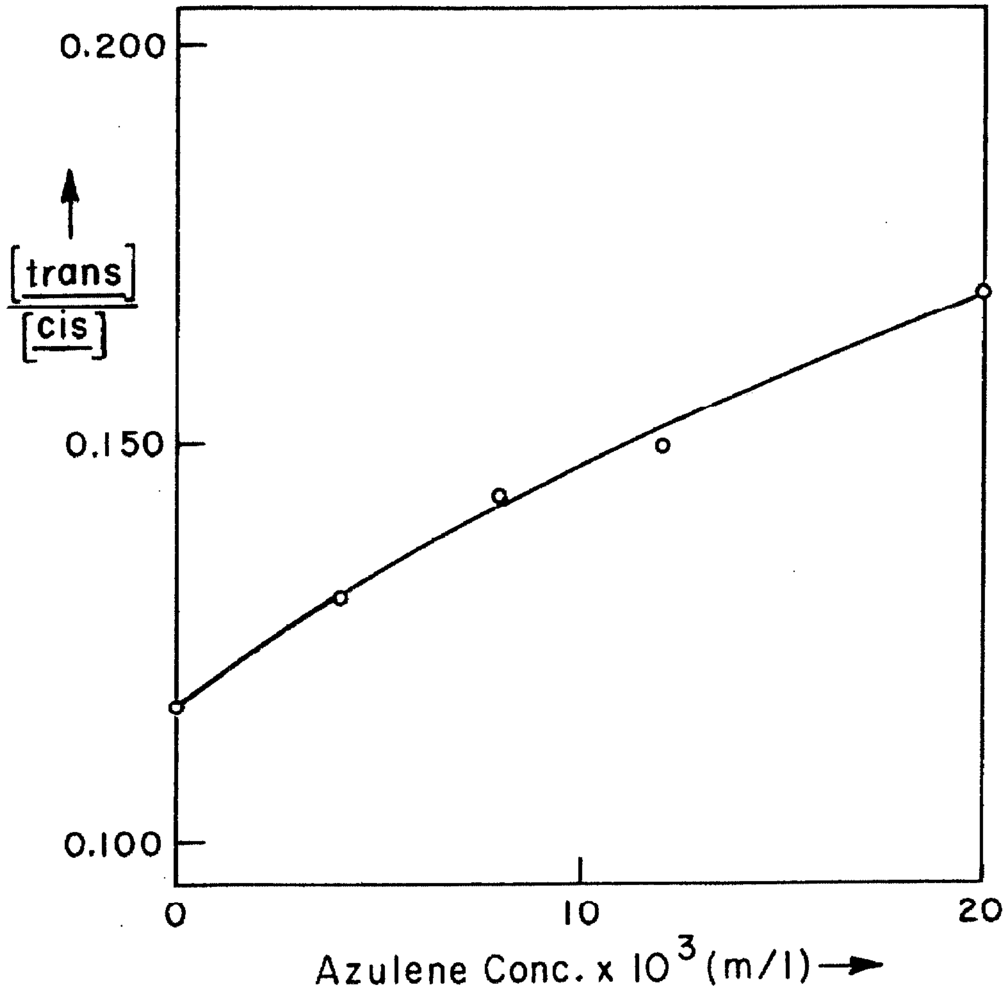
It was necessary to consider other steps in which azulene might be involved. The possibility that internal filtering by azulene could lead to larger concentrations of cis-stilbene than expected can be ruled out. The variation of the extinction coefficients of the stilbenes and azulene over the narrow band width of the exciting light used was negligible (see experimental). Two other possible complications involve energy transfer from stilbene singlet states to azulene or steps involving azulene and transient dihydrophenanthrene.

The best way to determine the effect of singlet energy transfer, if present, on the stilbene stationary states, would be to study this effect with a quencher which could not participate in any other energy transfer steps. Such a quencher is ferric dibenzoylmethide [$Fe(DBM)_3$]. Its ability to quench benzophenone singlets has been established unequivocally (35,61). Since the $S_1 \rightarrow S_0$ energy gaps in the stilbenes are greater than the gap for the corresponding transition in benzophenone, it should be possible for $Fe(DBM)_3$ to quench stilbene singlets on energetic grounds. Furthermore, since $Fe(DBM)_3$ does not affect the benzophenone stationary state (61), it was not expected to become involved in any steps involving the transfer of triplet state energy. As shown in Table 34, its presence did not affect the stationary state of the stilbenes in the unsensitized isomerization. This result probably indicates that a concentration effect involving singlet energy transfer from stilbene singlets to azulene is unlikely.

The effect of azulene on the formation of transient(s) was determined by measuring the increase of absorption at 4500 Å in the presence and in the absence of azulene. After correction for internal filtering by azulene, it was found that the increase of absorption at 4500 Å was 40 per cent greater in the presence of azulene. Furthermore, the rate of disappearance of absorption, after irradiation was interrupted, was considerably slower in the solution without azulene. The absorption loss did not follow first order kinetics in either case. These results are neither very well understood nor very well documented. The concentration of stilbene used (1.6×10^{-3}M) was too low and, as a result, the maximum change in optical density at 4500 Å was only 0.100 units. Thus, the rate of disappearance of absorption could not be measured accurately.

The fact that more transient is observed in the presence of azulene can be explained if it is assumed that it is formed electronically excited, and that reactions 57, 58, and 59 are competing paths

Fig. 12. Azulene Concentration Effect on Unsensitized Stilbene Isomerization.



$$\text{cis}^{**} \longrightarrow \text{DHP}^{**} \qquad (56)$$

$$\text{DHP}^{**} \longrightarrow \text{DHP} \qquad (57)$$

$$\text{DHP}^{**} + \text{Azulene} \longrightarrow \text{DHP} + \text{Azulene}^{**} \qquad (58)$$

$$\text{DHP}^{**} \longrightarrow \text{a } \underline{\text{trans}} + (1\text{-a})\underline{\text{cis}} \qquad (59)$$

for its decay. The double asterisks again indicate excited singlet states. The intermediacy of an electronically excited transient may account for part of the intense short-lived emission observed from cis-stilbene. The emission has a maximum at 4600-4700 Å (10, 67). Since the absorption maximum of the transient is at 4550 Å, some of the emission might easily be fluorescence from this species. Since some emission is observed at wavelengths shorter than 4550 Å, some other emitting source must also be present.

In any event, despite the crudeness of the results, there seems to be little doubt that at least part of the azulene concentration effect involves the transient. Since the transient thermally reverts to cis-stilbene, and since all measurements of the stilbene concentrations were made after its disappearance, its presence in larger amounts would lead to stationary states which are richer in cis-stilbene than one would expect if only equation 13 were considered.

The complex decay kinetics observed may be attributed either to experimental error or to the presence of more than one transient. More experiments along these lines should be profitable.

APPENDIX

TRIPLET STATE ENERGIES OF SENSITIZERS

The sources of sensitizer triplet state energies used in Figure 5 need some comment. In most cases these values refer to the maximum of the 0-0 band in phosphorescence spectra obtained by Mr. W. G. Herkstroeter and Mr. A. A. Lamola of these Laboratories. The spectra were recorded at 77°K for solutions of the sensitizers in a glass consisting of methylcyclohexane and isopentane (5:1 by volume). The phosphoroscopes used for these measurements have been described previously (54, 68). Values obtained in this manner are shown in Table 35. In all cases the materials described in the experimental of this thesis were used. It was found that phosphorescence spectra measured in EPA glass (diethyl ether, isopentane and ethanol, 5:5:2 by volume) were in general shifted to higher frequencies than spectra measured in hydrocarbon glasses. These shifts were larger for $n\rightarrow\pi^*$ triplet states than for $\pi\rightarrow\pi^*$ triplet states. Since the solvent effects by EPA glass can be complex, and since the isomerization experiments were usually carried out in nonpolar solvents, the triplet state energies obtained from phosphoresce spectra of the sensitizers in hydrocarbon glass solutions were preferred.

The triplet state energy of fluorenone (53.0 kcal/mole) was obtained from its absorption spectrum in ethyl iodide (see experimental)

Table 35. Triplet State Energies of Sensitizers.

Compound	E_T(kcal/mole)	Source
Acetophenone	73.6	Lamola (L)
Benzophenone	68.5	L
Thioxanthone	65.5	L
Anthraquinone	62.4	Herkstroeter (H)
Flavone	62.0	H
Michler's ketone	61.0	H
2-Naphthyl phenyl ketone	59.8	H
2-Naphthaldehyde	59.5	H
2-Acetonaphthone	59.3	H
1-Naphthyl phenyl ketone	57.5	H
1,4-Naphthoquinone	57.0	H
1-Naphthaldehyde	56.2	L
Biacetyl	54.9	H
2,3-Pentanedione	54.7	H
Benzil	53.7	H
α-Naphthil	55.3, 53.4	H
β-Naphthil	58.2, 53.8	H

and later from its weak phosphorescence spectrum (53.3 kcal/mole) in hydrocarbon glass at 77°K.

The value for 1,4-benzoquinone (50.0 kcal/mole) was estimated from its ethyl iodide absorption spectrum. The ethyl iodide spectrum obtained in this work was similar to that reported by Kuboyama (69).

Since enough duroquinone was not available for singlet-triplet absorption measurements, its triplet state energy was estimated by assuming it to be identical with the triplet state energies of 2,3-dimethyl-1,4-benzoquinone and 2,5-dimethyl-1,4-benzoquinone. Singlet-triplet absorption spectra of these compounds have been obtained in <u>n</u>-heptane (0-0 band at about 51.6 kcal/mole) (69).

The values for pyrene (48.0 kcal/mole) and for 1,2-benzanthracene (47.3 kcal/mole) were obtained from the literature (58). They refer to the maximum of the 0-0 band of their respective phosphorescence spectra (77°K, isopentane and methylcyclohexane glass, 1:4 by volume).

The value for eosin (43 kcal/mole) is from the phosphorescence spectrum of this compound in EPA glass at 77°K (70).

The value for 9,10-dibromoanthracene (40.2 kcal/mole) is from its singlet-triplet absorption spectrum at room temperature in carbon disulfide (71).

The value for acridine (45.3 kcal/mole) was obtained by Evans (11). It is taken from the singlet-triplet absorption spectrum of this compound in chloroform in the presence of a high pressure of oxygen.

Mr. A. A. Lamola has measured phosphorescence spectra of 4-acetylbiphenyl and 2-acetylfluorene. Triplet state energies of 67.5 kcal/mole and 64.1 kcal/mole were indicated for these two compounds, respectively. In view of the [*cis*]/[*trans*] stationary state ratios obtained with the stilbenes in the presence of these sensitizers, it becomes necessary to conclude that the triplet state energies are high and perhaps reflect the presence of impurities in these sensitizers. In agreement with this prediction are two facts. The first is that whereas the addition of maleic anhydride to benzene is sensitized by thioxanthone, it is not sensitized by 2-acetylfluorene (72). The second fact is that the triplet state energy of

4-benzoylbiphenyl (77°K, diethyl ether and ethanol, 1:2 by volume) was measured from its phosphorescence spectrum to be 60.6 kcal/mole (73). Since the energies of 2-acetonaphthone and 2-naphthyl phenyl ketone are essentially identical (see Table 35), it is likely that the energy of 4-acetylbiphenyl should be very close to 60.6 kcal/mole. This latter value is also predicted by the curve in Figure 5.

The value for the triplet state energy of 3-acetylpyrene was not measured, but in view of the fact that this sensitizer behaves with the stilbenes in precisely the same manner as acridine (see Fig. 7), a triplet state energy of 45.3 kcal/mole is predicted for this compound.

An attempt was made to measure singlet-triplet absorption from benzanthrone in ethyl iodide. Unfortunately, benzanthrone was relatively insoluble in this solvent, and it is likely that the shoulder observed at 51.0 kcal/mole does not correspond to the 0-0 band. A value of 46.0 kcal/mole was predicted for the 0-0 band of the phosphorescence spectrum of this sensitizer in order that its behavior with the stilbenes be in accord with the theory presented to explain Figure 5 and Figure 9. It should be pointed out that this value accurately predicts the behavior of benzanthrone as a sensitizer for other systems (74). Furthermore, it is in excellent agreement with the 0-0 band observed in the phosphorescence spectrum of

3-bromo-7-H-benz[de]anthracen-7-one (3-bromobenzanthrone) (45.7 kcal/mole) in heptane at 77°K (75).

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PROPOSITION I

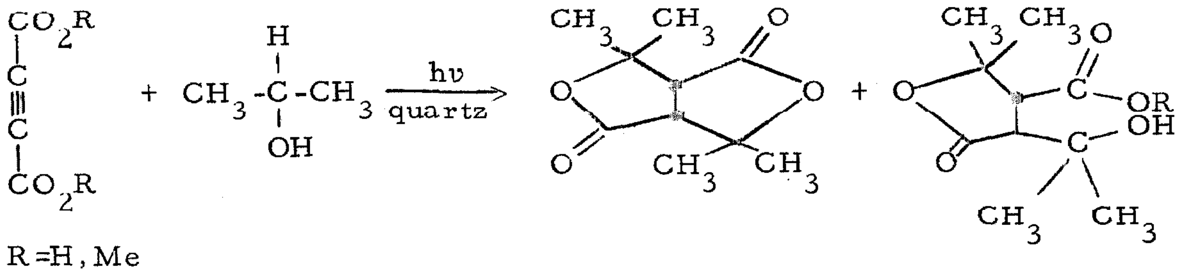
Chemical Spectroscopy Applied to Acetylenes

Experiments are described which should provide information about the geometry of the lowest triplet states of acetylenes.

Spectroscopic data (1, 2) as well as theoretical considerations (3, 4, 5) indicate very strongly that the lowest excited singlet states of acetylene and acetylene-d_2 have a trans-bent configuration. Presumably upon excitation $sp \rightarrow sp^2$ rehydridization occurs and the excited state can be crudely described as a ground state ethylene molecule with two hydrogen atoms removed. This enables the excited molecule to exist in either a cis or a trans configuration. The cis form is expected to be energetically less favorable because of greater orbital interaction in this geometry relative to the trans. This expectation has been confirmed both spectroscopically (i.e. no absorption that can be attributed to excitation of the linear ground state to a cis-bent excited state has been observed (4)) and by theoretical calculations (5).

No information of any kind is available about the energy or the geometry of the triplet states of acetylene. Furthermore, the effect of substituents on the geometry of the excited states of acetylenes has not been investigated.

Two experiments have come to attention, however, which indicate that an elegant approach to this problem is available. The first is the reaction, induced by light, between acetylenedicarboxylic acid (or the methyl diester) and isopropanol (6) (equation 1)



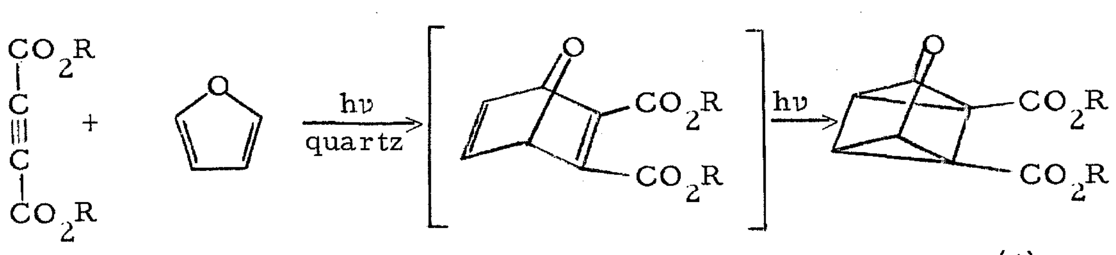
\+ other unidentified products

I

(1)

The importance of the reaction described in equation 1 is in that it suggests that some excited state of acetylene (singlet or triplet) can abstract hydrogen from a suitable source. The formation of the isolated products can be rationalized if it is assumed that the initial step involves the abstraction of a hydrogen atom from isopropanol by a <u>trans</u>-bent excited state of the acetylene.

A clue that <u>cis</u>-bent excited states of I may form under the conditions of the experiment described above is provided by reaction 2 (7). It is possible that the excited species which initiates reaction 2 is a



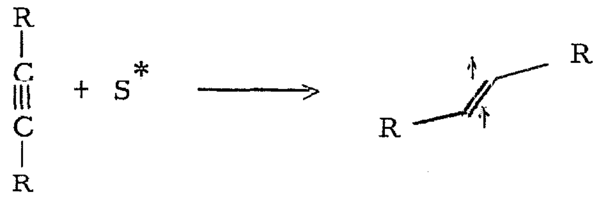
I

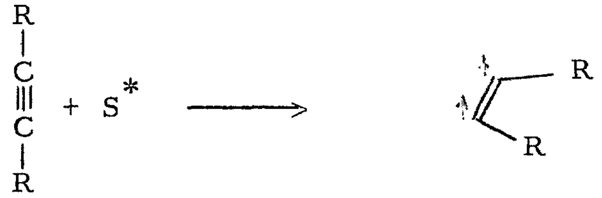
(2)

cis-bent excited state of the acetylene.

The multiplicity of the excited states involved in 1 and 2 is not known. Although it has been shown (8) that reaction 1 can be sensitized by benzophenone, this can be easily accounted for by a mechanism which does not involve triplet state acetylene as an intermediate.

It is proposed that the photochemical reduction of acetylenes to olefins may be effected by irradiation of the acetylenes in 1,4-cyclohexadiene in the presence of sensitizers which decay by way of triplet states. The reaction might proceed as is described in equations 3-8. The cyclohexadienyl radicals would be expected to either couple


(3)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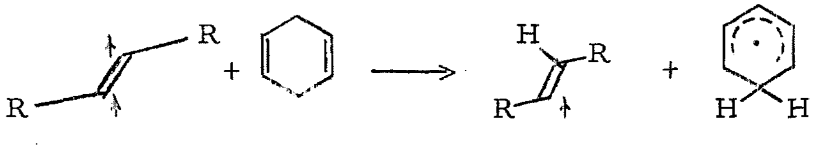
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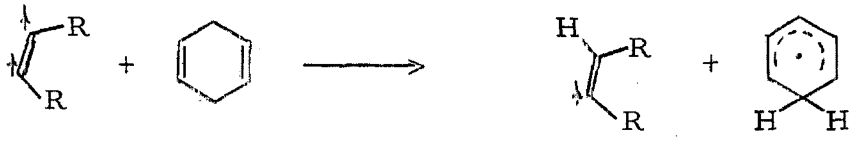
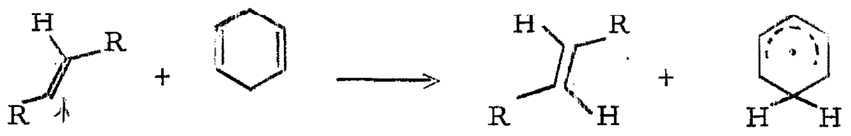
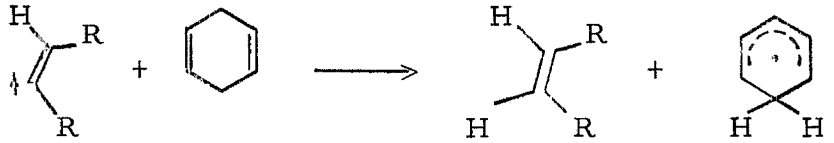

(6)



(7)



(8)

or disproportionate (9, 10). The [*trans*]/[*cis*] product ratio might then reflect the ratio of k_3 to k_4, which in turn might depend strongly upon the energy of the sensitizer. Variation of the product ratio, if present, should lead to an accurate estimation of $S_0 \rightarrow T_1$(*cis*-bent) and $S_0 \rightarrow T_1$ (*trans*-bent) excitation energies for acetylenic systems.

It should be pointed out that results from the proposed study might be complicated due to possible *cis-trans* isomerization of the vinyl radicals produced by reactions 6 and 7. A recent study involving the free radical addition of thiols to acetylenes (11) indicates that such an isomerization would be fairly facile. However, in the presence of excess hydrogen donor hydrogen abstraction competes favorably with this isomerization (11). An interesting feature of the proposed system is that in reactions 6 and 7 a vinyl radical and a cyclohexadienyl radical are produced in the same solvent cage. It is thus conceivable that a major product forming step might involve the disproportionation of the geminate radical pair prior to diffusive separation of the radicals.

The importance of vinyl radical isomerization can be evaluated by determining the variation of the product composition as a function of the concentration of hydrogen donor, 1,4-cyclohexadiene in an inert solvent, say benzene.

Clearly, the proposed study would be doomed unless at least some acetylenes have triplet state energies sufficiently low to permit use of suitable sensitizers. Evidence that the $S_0 \rightarrow T_1$ excitation energy of acetylenes might not be a severe limitation is available in the case of diphenylacetylene. The triplet state energy of this compound has been determined by measuring its $S_0 \rightarrow T_1$ absorption spectrum in chloroform under a high pressure of oxygen (12). The lowest energy band appears to be at about 62 kcal per mole, well within the range of available sensitizers.

It should be pointed out that for compounds such as diphenylacetylene the lowest triplet state may be linear. This case should also be reflected by the [cis]/[trans] product ratio as the sensitizer energy is varied.

Only sensitizers whose triplet states do not abstract hydrogen atoms will be suitable for this study.

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PROPOSITION II

Vapor Phase Photochemistry of Benzophenone

An alternate interpretation is proposed for a series of experiments involving the benzophenone sensitized phosphorescence of biacetyl in the vapor phase. Experiments are described which should distinguish between transfer of singlet and triplet excitation from benzophenone to potential acceptors in the vapor phase. Possible photochemical reactions of benzophenone in the vapor phase are considered.

Dubois has shown that absorption of light by benzophenone in the presence of biacetyl (both in the vapor phase) induces phosphorescence in biacetyl. The relative biacetyl phosphorescence intensities in the presence (P_A) and absence (P_{A_0}) of benzophenone were measured as a function of the concentrations of donor (D) and acceptor (A).

The results were explained by a mechanism which assumes that only triplet excitation transfer is involved. The steps considered important are shown in equations 1-9. The asterisk denotes an

$$^1D + h\nu \longrightarrow {}^1D^* \qquad (1)$$

$$^1D^* \longrightarrow {}^3D^* \qquad (2)$$

$$^3D^* \longrightarrow {}^1D \quad (3)$$

$$^3D^* + {}^1A \longrightarrow {}^1D + {}^3A^* \quad (4)$$

$$^1A + h\nu \longrightarrow {}^1A^* \quad (5)$$

$$^1A^* \longrightarrow {}^1A \quad (6)$$

$$^1A^* \longrightarrow {}^3A^* \quad (7)$$

$$^3A^* \longrightarrow {}^1A + h\nu \quad (8)$$

$$^3A^* \longrightarrow {}^1A \quad (9)$$

electronically excited state. This mechanism predicts that under photostationary state conditions the relative phosphorescence intensities of biacetyl will be given approximately by equation 10.

$$\frac{P_A}{P_{A_0}} = 1 + \frac{\epsilon_D}{\epsilon_A} \left\{ \frac{k_4[{}^1D]}{k_3 + k_4\,[{}^1A]} \right\} \frac{k_7 + k_6}{k_7} \quad (10)$$

In equation 10, ϵ_D and ϵ_A are the extinction coefficients of donor and acceptor at the wavelength of the incident light (2750 Å). The data could be fitted satisfactorily to equation 10 and the quantity k_4/k_3 was evaluated as 10^4. The rate of energy transfer, k_4, was estimated by assuming that transfer occurred on every collision and that the sum of the collision radii of biacetyl and benzophenone is 10 Å. This led to the conclusion that the mean lifetime of benzophenone triplets in the vapor phase is $\frac{1}{k_3} \approx 10^{-8}$ sec.

As evidence against the involvement of singlet excitation transfer Dubois points out that due to very rapid intersystem crossing, the excited benzophenone singlet state is not sufficiently long-lived to become involved in energy transfer processes. This is presumably confirmed by the results of Bäckström and Sandros (2), which indicate that for the same system (benzophenone, biacetyl) in benzene solution only triplet state energy transfer takes place. Actually, close examination of the results of Bäckström and Sandros reveals that due to the great efficiency of intersystem crossing in biacetyl, it should be very difficult to distinguish between the case of 100% triplet excitation energy transfer and the case where as much as 10% of the transfer process involves excited singlet states. Furthermore, for the similar donor-acceptor pair of benzophenone and anisil, it appears that the sensitized and the unsensitized emission from anisil contain almost identical amounts of fluorescence. Since there is good overlap between the expected fluorescence spectrum of benzophenone and the $S_0 \rightarrow S_1$ absorption spectrum of either biacetyl or anisil the total absence of singlet energy transfer in solution would be surprising. The usual explanation that due to exceedingly rapid intersystem crossing the lowest excited singlet state of benzophenone is not sufficiently long-lived to become involved in energy transfer processes is no longer valid. Recent results indicate that benzophenone is an effective donor of singlet excitation to ferric dibenzoylmethide in benzene solution (3). The above considerations added to the fact that singlet energy transfer seems to be the predominant process in the vapor phase for the donor-acceptor pair pentanone and biacetyl (4) suggest that the assumption that singlet energy transfer from benzophenone to biacetyl (both in the vapor phase) can be neglected is not entirely justified.

Assuming the mechanism described in equations 1-9, Dubois calculates a mean lifetime of 10^{-8} sec for benzophenone triplets. The directly measured mean lifetime of benzophenone triplets in solution is 10^{-5} sec(5). Such a decrease in triplet state lifetime on passing from the liquid phase to the vapor phase does not appear reasonable. For example, the lifetime of the triplet state of biacetyl is 1.5×10^{-3} sec (6) in the vapor phase and 0.8×10^{-3} sec (7, 8) in benzene solution.

It is proposed that the predominant path of energy transfer from benzophenone to biacetyl in the vapor phase involves singlet excitation. The mechanism may be described as shown below.

$$ {}^{1}D + h\nu \longrightarrow {}^{1}D^{*} \qquad (1)$$

$$ {}^{1}D^{*} \longrightarrow {}^{1}D \qquad (11)$$

$$ {}^{1}D^{*} \longrightarrow {}^{3}D \qquad (12)$$

$$ {}^{1}D^{*} + {}^{1}A \longrightarrow {}^{1}D + {}^{1}A^{*} \qquad (13)$$

$$ {}^{1}A^{*} \longrightarrow {}^{1}A \qquad (6)$$

$$^{1}A^{*} \longrightarrow {}^{3}A^{*} \qquad (7)$$

$$^{3}A^{*} \longrightarrow {}^{1}A + h\nu \qquad (8)$$

$$^{3}A^{*} \longrightarrow {}^{1}A \qquad (9)$$

$$^{1}A + h\nu \longrightarrow {}^{1}A^{*} \qquad (5)$$

It should be pointed out that the above mechanism also represents an extreme case, since triplet state energy transfer (equation 4) is totally neglected. Using steady-state kinetics, the following relationship is predicted by this mechanism:

$$\frac{P_A}{P_{A_0}} \simeq 1 + \frac{\epsilon_D}{\epsilon_A} \left\{ \frac{k_{13} [^1D]}{k_{11} + k_{12} + k_{13} [^1A]} \right\} \qquad (13)$$

Since equations 10 and 13 are formally identical (note that to a first approximation $\frac{k_7 + k_6}{k_7} = 1$), using the arguments of Dubois, the lifetime of the excited benzophenone singlet state $(k_{11} + k_{12})^{-1}$ is calculated to be about 10^{-8} sec. It should be pointed out that the calculation of this value involves the assumption that energy transfer occurs on every collision. Actually singlet energy transfer could occur over greater distances than the assumed 10 Å collision diameter. The value should be regarded as an upper estimate of the lifetime of the benzophenone singlet state. A lifetime slightly smaller than 10^{-8} sec is required by the fact that although the calculated radiative lifetime of the excited benzophenone singlet state is 2×10^{-7} sec (9), no fluorescence has been observed from benzophenone (i.e. $k_{11} \approx 2 \times 10^{-7}$ sec $<< k_{12}$).

Measurement of the lifetime of benzophenone triplets in the vapor phase should determine whether the present criticism of Dubois' mechanism is valid. It is proposed that quantum yields be determined for the benzophenone sensitized isomerization of trans-piperylene in the vapor phase as a function of piperylene concentration. In this case singlet energy transfer can be excluded on energetic grounds and the mechanism should involve triplet state excitation transfer upon every collision of triplet benzophenone and piperylene (10). In its simplest form the mechanism is described in the following equations where P denotes piperylene and all other symbols have their usual meaning.

$$^1D + h\nu \longrightarrow {}^1D^* \qquad (1)$$

$$^1D^* \longrightarrow {}^3D^* \qquad (2)$$

$$^3D^* \longrightarrow {}^1D \qquad (3)$$

$$^3D^* + {}^1t\text{-}P \longrightarrow {}^1D + {}^3D^* \qquad (14)$$

$$^3P^* \longrightarrow {}^1t\text{-}P \qquad (15)$$

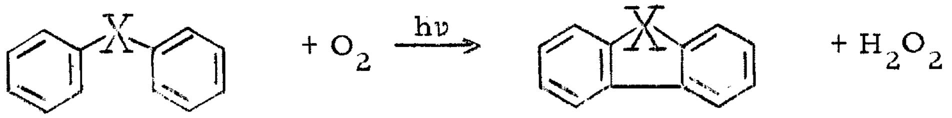
$$^3P^* \longrightarrow {}^1c\text{-}P \qquad (16)$$

The predicted dependence of the trans→cis quantum yield as a function of initial trans-piperylene concentration is shown in equation 17. Use of this equation should lead to the evaluation of k_3/k_{14} and

$$\frac{1}{Q_{t \to c}} = \frac{k_{15} + k_{16}}{k_{16}} \quad 1 + \frac{k_3}{k_{14}[{}^1t\text{-}P]} \qquad (17)$$

hence to an estimate of the lifetime of triplet benzophenone in the vapor phase.

Equation 17 is not exact, since it involves the assumption that the quantum yield for intersystem crossing of benzophenone is unity. Actually this quantity has been shown to be 0.94 (11) in solution and in the absence of singlet energy acceptors. The difference of this number and unity might be ascribed to at least two photoreactions of the excited singlet state. The first involves primary dissociation of benzophenone into phenyl and benzoyl radicals. This reaction would be especially important in the vapor phase. In fact, the phosphorescence spectrum ascribed to benzophenone vapor at 170° by Dubois (1) is not at all characteristic of benzophenone, but could be very nicely assigned to benzil. The second reaction which might be of importance in the vapor phase is the formation of fluorenone from benzophenone. Many examples of photooxidations in solution of the type shown in equation 18 are known (12, 13, 14). Such reactions in the vapor phase



(18)

can proceed in the absence of oxygen (15) (i.e. hydrogen is the other product) and the possibility that this process occurs with benzophenone should be examined.

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PROPOSITION III

The Wieland Reaction

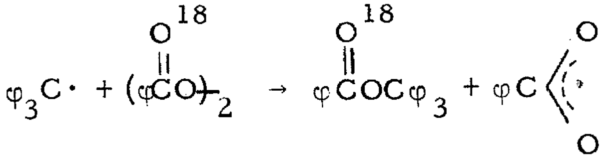
This proposition is concerned with the role of "free" benzoyloxy radicals in the Wieland reaction.

The reaction of triphenylmethyl radicals with benzoyl peroxide in aromatic solvents to yield triphenylmethyl benzoate, benzoic acid and substituted tetraphenylmethanes is known as the Wieland reaction (1, 2, 3, 4).

The overall reaction is represented by equation 1. The initial step

$$(BzO-)_2 + 2\,\varphi_3C\cdot + ArH \rightarrow \varphi_3COBz + BzOH + \varphi_3CAr \qquad (1)$$

involves attack by the triphenylmethyl radical on the peroxide oxygen (5), equation 2. It is generally agreed that reaction 2 as well as coupling



$$\varphi_3C\cdot + (\varphi\overset{O^{18}}{\overset{\|}{C}}O-)_2 \rightarrow \varphi\overset{O^{18}}{\overset{\|}{C}}OC\varphi_3 + \varphi C\langle^{O}_{O}\cdot \qquad (2)$$

of benzoyloxy radicals with triphenylmethyl radicals, reaction 3,

$$BzO\cdot + \varphi_3C\cdot \rightarrow \varphi_3COBz \qquad (3)$$

account for all the triphenylmethyl benzoate formed.

At least three mechanisms have been proposed to account for the formation of benzoic acid and tetraphenylmethanes. The first was proposed by Wieland (2, 3) and is represented by equations 4 and 5.

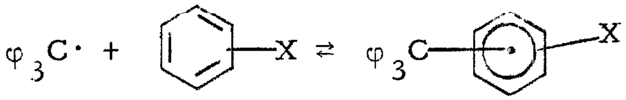
$$BzO\cdot + ArH \rightarrow Ar\cdot + BzOH \tag{4}$$

$$\varphi_3C\cdot + Ar\cdot \rightarrow \varphi_3CAr \tag{5}$$

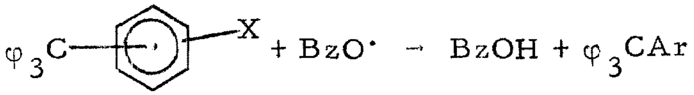
Hammond and coworkers (5) have pointed out that the absence of diphenyls among the products as well as the fact that when the Wieland reaction was carried out in toluene (3) no evidence for benzyl radicals was obtained , speak against the above mechanism. Instead, they suggest (4) that a concerted attack of a benzoyloxy and a triphenylmethyl radical upon the aromatic substrate, equation 6, might be involved.

$$\varphi_3C\cdot + ArH + BzO\cdot \rightarrow BzOH + ArC\varphi_3 \tag{6}$$

Recently Benkeser and coworkers (6) determined relative reactivities for the triphenylmethylation of several aromatic substrates. It was found that the reactivity of the triphenylmethyl radical toward aromatic rings was in the order: $\varphi OCH_3 > \varphi Cl > \varphi H > \varphi CO_2CH_3 > \varphi CF_3 >> \varphi NO_2$. Their results showed that triphenylmethylation is different from phenylation in at least two important respects: first, nitrobenzene, which is very reactive toward phenylation, is completely inert toward triphenylmethylation; second, whereas in phenylation one observes some directive substituent effects in the isomer distributions of the products (7), it was found that, for the substrates studied, triphenylmethylation led to little deviation from a statistically random isomer distribution. The observed order of reactivity was explained in terms of the ease of formation of a loose π-complex between triphenylmethyl radicals and the substrate. Their mechanism for triphenylmethylation is shown in equations 7 and 8.



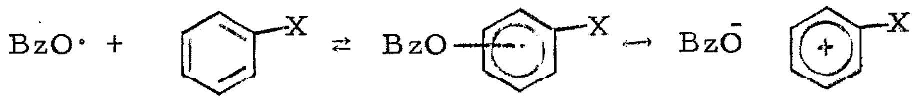
(7)



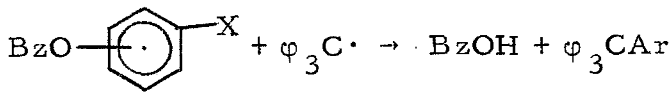
(8)

They suggested that in the case of unreactive substrates such as nitrobenzene complex formation between the substituent, X, and the triphenylmethyl radical favors reaction 3 over 7 and 8. Actually, existing evidence, although not as extensive as might be desired, suggests that complexes of the type shown in equation 7 are not involved. For example, the dissociation constant of hexaphenylethane is essentially the same when measured in dioxane, bromobenzene, ethylene bromide or benzene (8). Furthermore, it appears that nitrobenzene does not form complexes of any kind with triphenylmethyl radical since its addition to benzene solutions of the radical does not alter the absorption spectrum (9).

A mechanistic possibility which has thus far received little attention is shown in equations 9 and 10. In view of contributions from the



(9)



(10)

polar resonance structure shown in equation 9 one would expect that electron donating substituents would increase the stability of complexes between the benzoyloxy radical and aromatic substrates. This mechanism is thus in accord with the relative reactivities observed by Benkeser (6).

The fact that no carbon dioxide is formed in the Wieland reaction (4) indicates that the benzoyloxy radicals are intercepted prior to decarboxylation. Presumably, processes 6, or 7, 8, or 9, 10, if operative, are extremely fast. To determine the extent to which benzoyloxy radicals, at room temperature, can survive decarboxylation in the absence of such processes, it is proposed that the method of isotope dilution be used to determine the products from dilute solutions of triphenylmethyl radicals and benzoylperoxide in nitrobenzene. Under such conditions decarboxylation should be competing only with reaction 3.

Direct evidence for the intermediacy of complexes between benzoyloxy radicals with aromatic substrates might be obtained using flash spectroscopic techniques. It is proposed that the rate of disappearance of benzoyloxy radicals produced by flash photolysis of benzoyl peroxide be determined in several aromatic substrates. If complexes are involved, the absorption spectrum as well as the rate of disappearance of the benzoyloxy radicals should be solvent dependent.

Ideally, conditions should be chosen such that essentially all the benzoyl peroxide is decomposed with the first flash. If this is the case, complications that might arise from induced decomposition of the "remaining" peroxide may be avoided. A rather incomplete study of the benzoyl peroxide decomposition upon irradiation has been reported (10) but is not very informative.

Recently, the Wieland reaction has been extended to acyl peroxides (11). The results suggested that the extent of triphenylmethylation of the aromatic substrate is very sensitive to the stability of the acyloxy radical involved. The fact that of all the acyl peroxides used only cyclopropylformyl peroxide led to formation of detectable amounts of tetraphenylmethane was attributed to the greater stability of the cyclopropylcarboxy radical toward decarboxylation relative to simple acyloxy radicals. The extent of stabilization of acyloxy radicals by complex formation of the type shown in equation 9 should be reflected in greater yields of aryltriphenylmethanes in aromatic substrates with electron releasing substituents. It is proposed that this possibility be examined at least in the case of cyclopropylformyl peroxide.

A great deal of the early work on the Wieland reaction should be reexamined. It is intriguing, for example, that triphenylmethylation of cyclohexane can be effected (3). It is likely that this reaction can be correctly represented by the initial Wieland mechanism (analogous to steps 4 and 5). This leads one to suspect that triphenylation of toluene should lead to formation of at least some benzyl radicals; a reinvestigation of this system is therefore proposed. The relative rates of hydrogen abstraction by benzoyloxy radicals and participation in the triphenylmethylation of aromatic substrates should be reflected by the products formed when the Wieland reaction is carried out in mixtures of cyclohexane and benzene.

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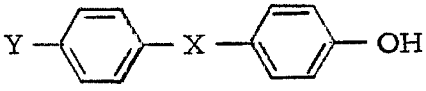
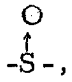
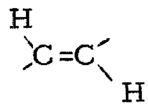
PROPOSITION IV

Sulfur d-Orbital Interaction

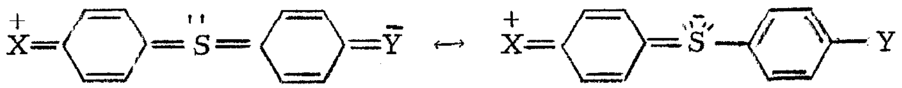
It is proposed that determination of Hammett ρ values for the ionization of phenols of type I, where Y- is some substituent and -X-



I

is -O-, -S-,  $-\overset{\overset{O}{\uparrow}}{S}-$,  $-\underset{\underset{O}{\downarrow}}{\overset{\overset{O}{\uparrow}}{S}}-$ and  $\overset{H}{\diagdown}C=C\underset{H}{\diagdown}$, will permit an estimation of the extent to which d-orbitals participate in transmitting electronic effects through sulfur.

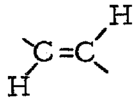
Extensive ultraviolet spectrophotometric studies of diaryl sulfides (1, 2) were interpreted to indicate that the aryl substituents are isolated. It was concluded that conjugation through sulfur (type II) was not important, but that conjugation of the type III could not be ruled

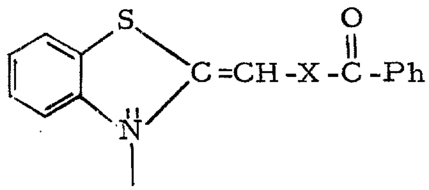


II

III

out. Similar studies of aryl vinyl sulfides (3) substantiate these results.

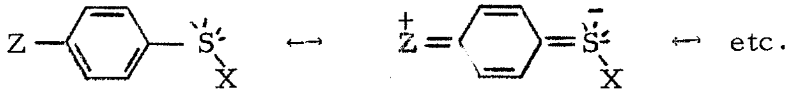
Although most spectral evidence indicates that structures in which sulfur is flanked by two double bonds (II) are not important (4), such structures have on some occasions been proposed (5, 6, 7). For example, it was found (5) that bathochromic shifts occur in the spectra of dyes of the type IV as -X- is changed from -O- to -S- to  $\overset{}{\underset{H}{>C}}=\overset{H}{C}<$ (see below). It was suggested that this shift indicates that sulfur can transmit electronic effects but that it does so much less effectively than a double bond.



IV

X	O	S	$\overset{H}{C}=\underset{H}{C}$
λ (mμ)	307	385	481
log ε	3.67	3.72	4.66

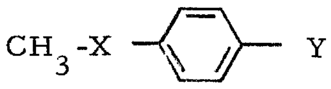
Substitution of electron withdrawing groups on sulfur is believed to cause a contraction of its vacant 3-d-orbitals; this contraction increases their ability to form bonds (4). For example, it has been pointed out (8, 9) that when sulfur is involved in compounds such as V, where Z is an electron-donating substituent, resonance structure VI



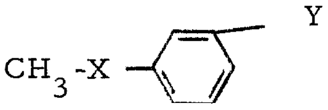
V VI

should become more important as the electron withdrawing ability of group X is increased. That this is the case was demonstrated (8) by an analysis (based on the σ_R parameters of Taft and Lewis (10)) of the ionization constants of acids, V, (Z=CO_2H) and phenols, V, (Z=OH) where -X was $-CH_3$, $-COCH_3$, and -CN.

Because oxygen is electron withdrawing, its addition to the sulfur of diaryl sulfides to yield sulfoxides and sulfones should lead to corresponding increases in the ability of sulfur to utilize its d-orbitals. Bordwell and coworkers (11, 12) have studied the systems VII and VIII where X was either $-\overset{O}{\overset{\uparrow}{S}}-$ or $-\overset{O\ \ O}{\overset{\uparrow\nearrow}{S}}-$ and Y was $-CO_2H$ and OH. It was

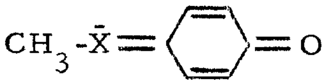


VII



VIII

suggested (11) that the difference between the σ-constants of para substituents for benzoic acids and phenols might be taken as an indication of the extent of conjugation of type IX, since similar structures

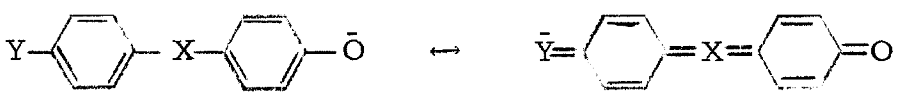


IX

cannot be written for the anion of the analogous acid. It was concluded that structures IX were important in both sulfoxide and sulfone.

As an extension of the above investigations, it is proposed that a determination of Hammett's (13) reaction constants, ρ, for the ionization of phenols of type I be carried out where Y is some substituent and -X- is -O-, -S-, $-\overset{O}{\overset{\uparrow}{S}}-$, $-\overset{O\ \ O}{S}-$, or $\overset{H}{C}=\underset{H}{C}$. The ρ values may be used as a measure of the efficiency of the group X in transmitting electronic effects.

The relative importance of resonance structures X in the above systems might be deduced from the results obtained for substituents,



etc.

X′

Y, which require σ^* values (13) when p-substituted phenols of type XI are fitted to the Hammett equation. Since X′ will be important (13, 14)

XI

when X is $\underset{H}{C}=\overset{H}{C}$, it is expected that for this system substituents Y such as NO_2, CHO, and CN will require σ^* values in order that they fit the Hammett equation. The contribution of resonance structure X will be negligible when -X- is -O- and it might be reasonable to expect that σ values will be required for all the substituents in this system. The position of the other three groups, X, between the two extreme cases just described, might similarly reflect the extent of direct conjugation through these groups.

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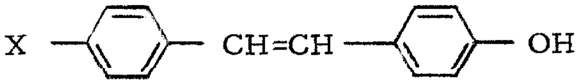
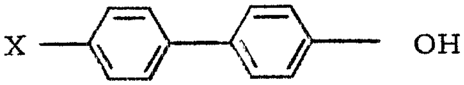
APPENDIX TO PROPOSITION IV

The proposed study will lead to meaningful results provided the ρ for the dissociation constants of p'-substituted p-hydroxystilbenes (I) is large.



I

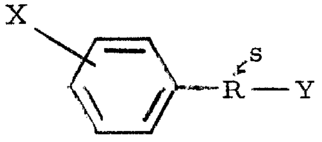
A prediction of the ρ for the dissociation constants of compounds I can be made by assuming that the substituent effect fall-off factor across a phenyl group will be very similar to the fall-off factor across a styryl group. In the case of m'- and p'-substituted biphenyl-p-carboxylic acids a fall-off factor of 0.37 has been observed (1). Since ρ for the dissociation constant of phenols is about 3 (2), one would expect a ρ of about 1 for the dissociation constants of m'- and p'-substituted p-hydroxybiphenyls (II).



II

It is felt that dilution of substituent effect due to the increase of the distance between the substituent and the reaction site in compounds of type I relative to compounds of type II, will be approximately offset by the greater p-orbital overlap which can be attained in the former system.

A semi-quantitative method for comparing fall-off factors for different groups R for compounds of type III, where X is the substituent



III

and Y is the reaction site, has been suggested by Jaffe (3). Three assumptions were involved:

1) Substituents induce changes in the electron density at the meta and para positions of a benzene ring which are proportional to corresponding σ -values.

2) Change of electron density induced by a substituent on a carbon in the benzene ring is independent of a side chain attached to that atom.

3) In III the effect of X on the carbon atom attached to Y (i.e., s) is independent of Y and depends only on the charge density that is induced by X on s.

These assumptions, when used to compare ρ 's for the dissociation constants of compounds I and II, lead to equation 1, where $q_s(X)$ and

$$\rho_I/\rho_{II} = \frac{q_s^{I}(X) - q_s^{I}(II)}{q_s^{II}(X) - q_s^{II}(H)}$$

$q_s(H)$ are electron densities at atom s in the substituted and unsubstituted compounds I and II.

A zeroth-order LCAO-MO calculation was used to estimate the electron densities in equation 1. Since the ratio of the ρ's is independent of the substituent X, the coulomb and resonance integrals chosen for this substituent should not affect the ratio. For this reason, the two substituents X that were considered were assigned the values for oxygen and nitrogen suggested by Roberts (4). Resonance integrals were calculated by assuming the bond distances and bond angles as determined in the vapor phase for biphenyls (5) and in the crystal for trans-stilbene (6). The methods described by Roberts (7) were used in these calculations. The auxiliary inductive parameter (8), $\delta = 1/3$, was used to calculate the carbon coulomb integrals, mainly because this value appeared to be most successful in Jaffe's treatment (3). To determine the effect of variation of this parameter, calculations were also made using $\delta = 1/10$. The results obtained are tabulated below (9).

Calculated Relative Fall-Off Factors

X	α_x	β_x	δ	ρ_I/ρ_{II}
N	$\alpha_c + \beta_{cc}$	β_{cc}	1/3	1.15
			1/10	1.14
O	$\alpha_c + 2\beta_{cc}$	$\beta_{cc}\sqrt{2}$	1/3	1.13
			1/10	1.11

The agreement between the values obtained is remarkable. The ratio of about 1.1 for ρ_I/ρ_{II} is certainly in agreement with the prediction made in advance of these calculations. It should be pointed out, however, that the assumptions involved in obtaining the above ratio are questionable. Furthermore, although the results suggest that the substituent effect through the phenyl moiety is smaller than the effect through the styryl moiety, the values predicted for the ratio of either ρ_I or ρ_{II} to the ρ of substituted phenols were smaller by a factor of three than those expected.

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9. Thanks are due to Mr. R. P. Foss for help in the use of the IBM 7090 computer program.

PROPOSITION V

Phosphorescence from Olefins

Systems are suggested to test the proposed explanation (1) for absence of phosphorescence from olefins.

As has been pointed out in this thesis (2), no triplet-singlet emission has ever been observed from olefins. An explanation for this lack of phosphorescence has been proposed by Potts (1). This author suggests that, at least for alkyl substituted olefins, Mulliken's and Roothaan's (3) calculations indicate that the potential energy curves for twist about the central bond of the ground singlet and the lowest triplet states intersect. Radiationless cross-over to the ground state occurs very rapidly at this intersection, and due to the long radiative lifetimes of the olefinic triplet states involved, phosphorescence is not a competitive decay process. Phosphorescence should be observed from olefins for which the potential energy surfaces of the triplet state and the ground state do not cross due to barriers to rotation about the double bond. For example, Potts (1) predicts that cyclohexene should phosphoresce.

In this thesis, the 0-0 band of the phosphorescence spectrum of trans-stilbene was predicted to be at about 46 kcal per mole.

Confirmation of this prediction by spectroscopic means would be highly desirable, since it would add considerable weight to the speculative hypothesis that when the energies of acceptor-donor pairs approach one another, the efficiency of energy transfer becomes very sensitive to exact matching of 0-0 bands (2).

The photochemical data for stilbene isomerization has been interpreted to indicate that a shallow minimum exists in the potential energy surface of the lowest triplet state at a configuration which is at least close to *trans* planar. It is therefore reasonable to expect that if the *trans* triplet state were to be populated at a very low temperature (say 4°K), the barrier for twisting about the central bond should be sufficiently high to prevent rotation to the perpendicular triplet and thus eliminate fast radiationless decay to the ground state by Potts' mechanism.

Dyck and McClure's (4) study of temperature dependence for quantum yields of fluorescence and *trans*→*cis* isomerization was interpreted to suggest that the population of the triplet state of *trans*-stilbene would be extremely inefficient by direct absorption of light at low temperatures due to an energy barrier to intersystem crossing from the lowest excited singlet state. This does not appear to be the case for *trans*-4-bromostilbene. It is therefore proposed that *trans*-4-bromostilbene will phosphoresce at 4°K. Furthermore, it should be possible to induce phosphorescence from unsubstituted *trans*-stilbene at 4°K by populating its triplet state indirectly by energy transfer from benzophenone.

A further system which would be of interest is 1,2-diphenylcyclopentene. In the triplet state of this compound, the phenyl groups would be constrained close to a cis planar configuration and phosphorescence from this system might be similar to that which might be expected from cis-stilbene (5). Some experimental indication that this system should phosphoresce is available. 1,2-Diphenylcyclopentene may be regarded as a "chromophore" in 2,3-diphenylindenone. Phosphorescence has been observed from the latter compound at 77°K (6). Perhaps fortuitously the 0-0 band of this phosphorescence is found at 57 kcal per mole. This is precisely where cis-stilbene would be expected to phosphoresce (2,7).

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