Intra- *vs.* Intermolecular Olefin Interactions with the Phenyl Singlet and Triplet Excited States in Solution. A Comparative Study of 1-Phenyl-2-butene Photoisomerization, Toluene Photosensitized Isomerization of 2-Heptene, and the Quenching of the Fluorescence of Benzenoid Aromatics by Olefins[1,2]

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Abstract: 1-Phenyl-2-butene has previously been shown to undergo cis ⇄ trans photoisomerization upon irradiation in solution with 254-nm light. Intramolecular triplet energy transfer was proposed. The photochemical and photophysical properties of this compound have now been studied further and compared with those of toluene and toluene–heptene mixtures. The fluorescence of 1-phenyl-2-butene is similar in shape to, and slightly less intense than, that of toluene; by contrast, no phosphorescence emission could be detected from the aryl olefin. Singlet lifetimes for the two compounds have been calculated from oxygen quenching data and these, as well as other photophysical properties of the singlet state, have comparable values. Quantum efficiencies for the toluene-sensitized isomerization of 2-heptene ($\phi_{t\to c} = 0.16$; $\phi_{c\to t} = 0.14$) are similar to those for the phenylbutene ($\phi_{t\to c} = 0.20$; $\phi_{c\to t} = 0.16$) as are the calculated olefin triplet decay ratios. The photostationary state ($[O_c]_{pss}/[O_t]_{pss}$) for the toluene–heptene system is 0.742. It is proposed that only minor aryl olefin interactions exist in the phenylbutene ground and excited singlet states but that the previously proposed energy transfer in the triplet excited state is efficient and rapid. The previously estimated rate constant for this internal triplet transfer step has been revised upward to $\geq 3.6 \times 10^9$ sec^{-1} The fluorescence emission of both toluene and 1-phenyl-2-butene is quenched by piperylene at a rate close to diffusion controlled.

Recently we reported on the photolysis of 1-phenyl-2-butene in hydrocarbon solvents, whereby irradiation with 254-nm light results in cis–trans isomerization about the double bond.[3] The reaction was found to be clean, intramolecular in nature, and relatively efficient ($\phi_{t\to c} = 0.20$, $\phi_{c\to t} = 0.16$). It has been our thesis that this reaction could be viewed as a consequence of intramolecular triplet–triplet energy transfer with the primary steps being (1) excitation of the phenyl moiety, viewed in the first approximation as a chromophore insulated from the olefin linkage, (2) intersystem crossing to a phenyl triplet, (3) intramolecular triplet–triplet energy transfer to the olefin, and (4) decay of the olefin triplet to *cis*- or *trans*-1-phenyl-2-butene (the photostationary state is 1.19).

The present paper describes studies initiated with the purpose of refuting or corroborating this mechanistic scheme. Additional spectroscopic and chemical data have been gathered with particular attention devoted to the quenching of phenylbutene isomerization by *cis*-piperylene.[3] During the earlier stages of our studies, it was reported that fluorescence from naphthalene is efficiently quenched by olefins,[4] and it was clearly necessary to ascertain the extent to which such singlet quenching is a factor for simple benzenoid aromatics in solution. We have also examined the photochemistry and luminescence of toluene–olefin mixtures in order to establish an intermolecular model for the intramolecular system under study.

Results

A. Luminescence Experiments. The fluorescence spectra of *trans*-1-phenyl-2-butene (4.7×10^{-3} *M*) and toluene (5.0×10^{-3} *M*) were determined in cyclopentane solution at 25° and the corrected spectra are displayed in Figure 1. The general shape and wavelength of maximum emission for both compounds agree with the reported fluorescence spectrum of toluene.[5–8] The fluorescence and absorption spectra of phenylbutene exhibit good mirror image symmetry and the excitation and absorption spectra are virtually identical. The relative quantum efficiencies of fluorescence were calculated from the area ratio (solutions were of equal absorbance) with ϕ_f for 1-phenyl-2-butene found to be 79% that of toluene. This reduction is primarily a consequence of the increased alkyl chain length since *n*-butylbenzene shows a relative fluorescence efficiency of 82% with respect to toluene.[9] If one assumes[10] that ϕ_f for toluene is 0.10, ϕ_f for 1-phenyl-2-butene is calculated as 0.08.

Attempts were made to observe phosphorescence emission for 1-phenyl-2-butene at 77°K in isopentane and in ethanol. No such emission could be detected although we estimate emission of 2% or more relative to that of toluene would have been observed.

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[1] Organic Photochemistry. XIV. Part XIII: R. Brainard and H. Morrison, *J. Amer. Chem. Soc.*, **93**, 2685 (1971).

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[4] (a) L. M. Stephenson, D. G. Whitten, G. F. Vesley, and G. S. Hammond, *ibid.*, 88, 3665 (1966); (b) L. M. Stephenson, D. G. Whitten, and G. S. Hammond, "The Chemistry of Ionization and Excitation," G. R. A. Johnson and G. Scholes, Ed., Taylor and Francis, Ltd., London, 1967; (c) L. M. Stephenson and G. S. Hammond, *Pure Appl. Chem.*, **16**, 125 (1968).

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[6] J. B. Birks, C. L. Braga, and M. D. Lumb, *Proc. Roy. Soc., Ser. A*, 283, 83 (1965).

[7] J. W. Longworth and F. A. Bovey, *Biopolymers*, 4, 1115 (1966).

[8] I. B. Berlman, "Handbook of Fluorescence Spectra of Aromatic Molecules," Academic Press, New York, N. Y., 1965.

[9] P. Froehlich, unpublished data.

[10] H. M. Rosenberg and S. D. Carson, *J. Phys. Chem.*, **72**, 3531 (1968).

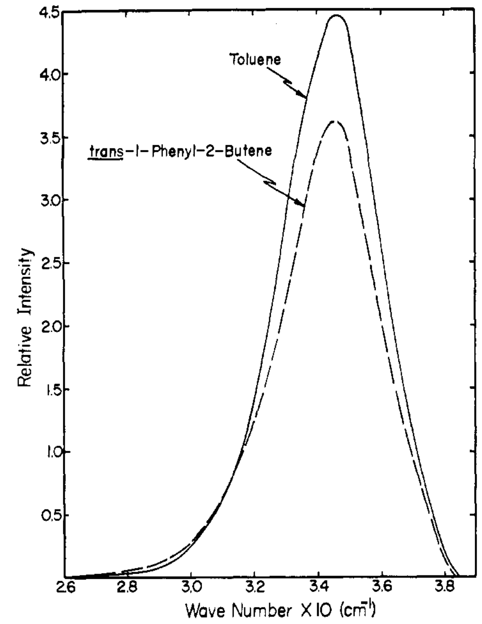

Figure 1. Corrected fluorescence spectra of *trans*-1-phenyl-2-butene and toluene in cyclopentane solution (25°).

B. Fluorescence Quenching. Addition of either 2-hexene or *cis*-piperylene to cyclopentane solutions of toluene and 1-phenyl-2-butene results in marked quenching of fluorescence emission. The data for *trans*-2-hexene are plotted in the usual Stern–Volmer fashion in Figure 2; the results for *cis*-piperylene are presented in Figure 3. Slopes were calculated by least-squares analysis of the data and are presented in Table I (also included in the table is the slope for quenching of *trans*-phenylbutene by *cis*-hexene). As one would expect, the presence of oxygen in the solutions shortened the lifetimes of the hydrocarbons and thus reduced the quenching efficiency of piperylene. When air was bubbled into the cyclopentane solutions in the absence of piperylene (oxygen concentrations estimated[11] at 2×10^{-3} *M*), ϕ_0/ϕ values for toluene and the phenylbutene were measured as 1.61 and 1.82, respectively.

Table I. Stern–Volmer Slopes for the Quenching of Toluene and 1-Phenyl-2-butene Fluorescence by Olefins[a]

Quencher	Slope, M^{-1}	
	Toluene	*trans*-1-Phenyl-2-butene
cis-Piperylene	151.3 ± 2.5	120.4 ± 2.6
cis-Piperylene (air saturated)	57.1 ± 1.6	46.3 ± 6.0
trans-2-Hexene	0.293 ± .077	0.164 ± 0.076
cis-2-Hexene		0.342 ± 0.090

[a] All data are for cyclopentane solutions at 25° with substrate concentrations *ca.* 5×10^{-3} *M*. Solutions were deaerated with nitrogen unless otherwise noted.

C. Photoisomerization of *trans*-1-Phenyl-2-butene as a Function of Wavelength. The quantum efficiency for trans → cis isomerization using 254-nm light is[3] 0.20. We have used a Bausch and Lomb "High Intensity" monochromator to determine quantum efficiencies at 246 ± 11 and 262 ± 11 nm to determine the effect of irradiation in other portions of the "B" absorption bond. Observed efficiencies were $\phi_{246} = 0.13$ and $\phi_{262} = 0.25$; *i.e.*, the quantum efficiency decreases at high frequencies of irradiation. This is the same trend that we have observed for 1-phenyl-1-butene[2b] photoisomerization but is opposite to the observations made on 6-phenyl-2-hexene photocycloaddition.[12]

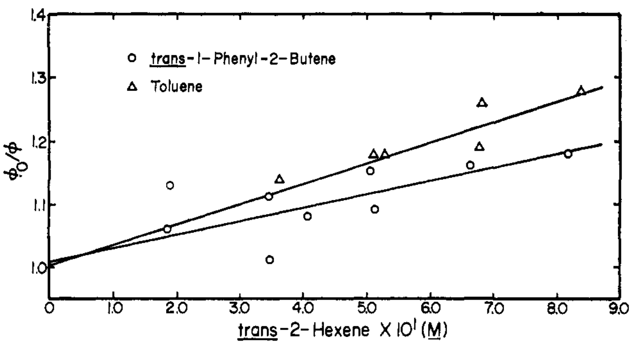

Figure 2. *trans*-2-Hexene quenching of the fluorescence of *trans*-1-phenyl-2-butene and toluene in cyclopentane solution (25°).

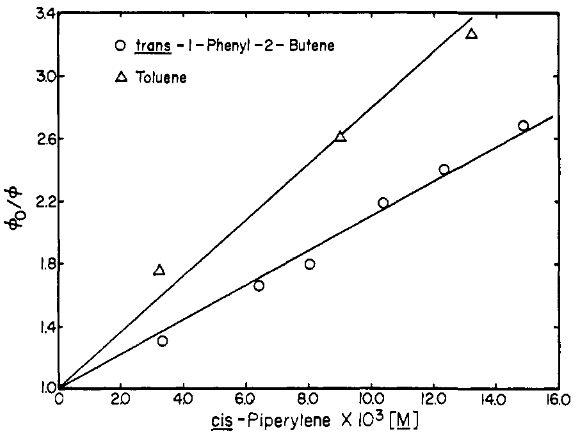

Figure 3. *cis*-Piperylene quenching of the fluorescence of *trans*-1-phenyl-2-butene and toluene in cyclopentane solution (25°).

D. Photoisomerization of *trans*-1-Phenyl-2-butene as a Function of Concentration. Toward completion of this work, a paper appeared[13] in which a concentration dependence is reported for 1-phenyl-2-butene photoisomerization. We examined two solutions of the trans isomer, one 7.07×10^{-3} *M* and one 25.5×10^{-3} *M;* quantum efficiencies measured were 0.20 and 0.22, respectively. These data are within experimental error of our previous observation[3] of $\phi = 0.20 \pm 0.01$ at 19×10^{-3} *M* but contrast with the factor of 2 change in ϕ reported[13] over this concentration range. Our values have been corrected for back-reaction.

E. Toluene- and Benzene-Sensitized Isomerization of 2-Heptene. The toluene-sensitized isomerization of 2-heptene was chosen as a suitable intermolecular analog for the 1-phenyl-2-butene molecule. The quantum yields for trans to cis and cis to trans isomerization are summarized in Table II. The quantum yields observed are $\phi_{t\rightarrow c} = 0.16$, $\phi_{c\rightarrow t} = 0.14$. These data appear to be independent of the concentration of toluene and, within the limited range studied, also inde-

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[11] J. C. Gjaldbaek, *Acta Chem. Scand.*, **6**, 23 (1952); J. H. Hildebrand and R. L. Scott, "The Solubility of Non-electrolytes," 3rd ed, Reinhold, New York, N. Y., 1950, p 243.

[12] W. Ferree, Jr., Ph.D. Thesis, Purdue University, 1971.

[13] C. S. Nakagawa and P. Sigal, *J. Chem. Phys.*, **52**, 3277 (1970).

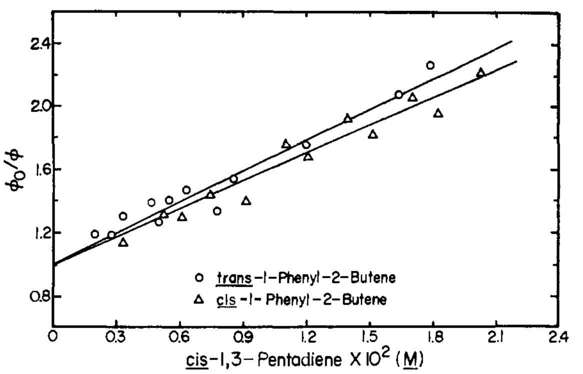

Figure 4. *cis*-Piperylene quenching of the photoisomerization of 1-phenyl-2-butene.

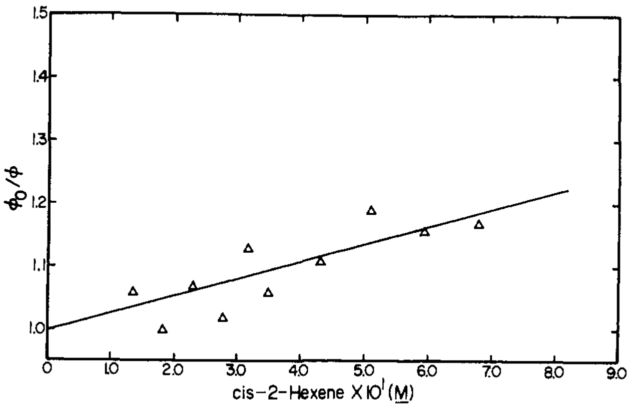

Figure 5. *cis*-2-Hexene quenching of the photoisomerization of *trans*-1-phenyl-2-butene.

pendent of olefin concentration. The first observation is of particular import since toluene excimer formation occurs at concentrations higher than *ca.* 0.5 *M*.[14] It would seem that formation of such excimers has no obvious effect on the ability to toluene triplets to transfer their triplet energy to an acceptor. Sato[15] has reported $\phi_{t \to c}$ and $\phi_{c \to t}$ for the sensitized isomerization of 2-butene in cyclohexane solution by a sensitizer of triplet energy equal to 83 kcal/mol (toluene?). His values are 0.13 and 0.16, respectively.

Table II. Quantum Yields for the Toluene-Sensitized Isomerization of 2-Heptene[a]

Toluene concn, *M*	Original isomer, *M*	Quantum yield,[b] mol einstein^{-1}
	Trans (0.10 *M*)	
2.04 × 10^{-2}		0.14
1.01 × 10^{-1}		0.15
4.81 × 10^{-1}		0.16
1.02		0.17
1.49		0.15
2.01		0.17
3.99		0.17
5.44		0.16
	Trans (0.22 *M*)	
5.24 × 10^{-1}		0.16
2.01		0.18
	Av	0.16 ± 0.01[c]
	Cis (0.10 *M*)	
2.14 × 10^{-2}		0.13
2.29 × 10^{-1}		0.14
2.01		0.15
	Av	0.14 ± 0.01[c]

[a] Cyclopentane solutions at 25.4 ± 0.6°. [b] Corrected for back-reaction where necessary. [c] Standard deviation.

Table III. Quantum Yields for the Benzene-Sensitized Isomerization of *trans*-2-Heptene[a]

Benzene concn, *M*	Quantum yield,[b] mol einstein^{-1}
5.27 × 10^{-1}	0.079
1.01	0.10
1.05	0.09
2.00	0.12
2.00	0.11
3.99	0.13
Av	0.10 ± 0.016[c]

[a] Cyclopentane solutions, 25.4 ± 0.6°, heptene concentration = 0.10 *M*. [b] Corrected for back-reactions where necessary. [c] Standard deviation.

For purposes of comparison, a more limited study was made of the benzene-sensitized isomerization of *trans*-2-heptene and the data are presented in Table III. The quantum yield we observe (0.10) is larger than the value of 0.03 reported by Sato[15] for the isomerization of *trans*-2-butene in cyclohexane using an 84 kcal/mol (benzene?) sensitizer.

The photostationary state for the toluene-sensitized isomerization of 2-heptene was determined by approach from both sides of the final value. The data are presented in Table IV. No comparable data for the sensitization of a monoolefin by toluene, in solution, could be found in the literature. The benzene-sensitized photostationary state of 2-heptene has been reported[16] to be 1.0. We have repeated this experiment and observe a confirmatory value of 1.04.

Table IV. Photostationary State of the Toluene-Sensitized Isomerization of 2-Heptene[a]

Initial isomer composition	$(\text{Cis})_{\text{pss}}/(\text{Trans})_{\text{pss}}$
68% trans, 32% cis	0.745
64% trans, 36% cis	0.731
58% trans, 42% cis	0.738
50% trans, 50% cis	0.754
Av	0.742 ± 0.0098[b]

[a] Cyclopentane solution, 25.0 ± 0.1°, toluene *ca.* 1.0 *M*, 2-heptene *ca.* 0.1 *M*. [b] Standard deviation.

F. Quenching of 1-Phenyl-2-butene Isomerization. In our previous paper[3] Stern-Volmer plots were presented for the quenching of *trans*-1-phenyl-2-butene photoisomerization by *trans*-2-hexene and *cis*-piperylene. We have extended these studies to include quenching of the trans isomer by *cis*-2-hexene and quenching of the cis isomer by piperylene. Figure 4 shows the piperylene quenching data for both phenylbutene isomers. Figure 5 displays the plot for *cis*-2-hexene quenching of the trans to cis isomerization. The slopes with piperylene are 65.0 ± 4.8 (M^{-1}) and 60.9 ± 4.5 (M^{-1}) for the *trans*- and *cis*-phenylbutene isomers, respectively.[17] The least-squares analysis of

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[14] P. K. Ludwig and C. D. Amata, *J. Chem. Phys.*, **49**, 326 (1968), and references therein.

[15] S. Sato, *Pure Appl. Chem.*, **16**, 87 (1968).

[16] M. A. Golub, C. L. Stephens, and J. L. Brash, *J. Chem. Phys.*, **45**, 1503 (1966).

[17] The figure of 65.0 for the trans isomer corrects a previous[3] value of 79.6 calculated with an extinction coefficient of 8.4 at 254 nm for

the data in Figure 5 yields a slope of 0.300 ± 0.059 (M^{-1}).

G. Photoisomerization of *cis*-Piperylene by Direct Irradiation. Despite the extensive use of piperylene as a triplet quencher[18,19] and triplet counter,[20] only upon completion of this work did the quantum efficiency for piperylene cis–trans isomerization by direct irradiation become available.[21] A determination of this number was made necessary by our use of the triplet counting technique[20] in a system involving light absorbed, in part, by piperylene and in which small quantum efficiencies of piperylene triplet formation is observed (see **F**). The quantum efficiencies which we have observed for cis → trans isomerization of piperylene using 254-nm light are 0.083, 0.086, and 0.094 (av $\phi_{c\rightarrow t}$ = 0.087).[22] The data were calculated using an extinction coefficient of 15 at 254 nm for freshly purified *cis*-piperylene.[23] This efficiency is consistent with that recently reported[20] and is by no means insignificant; whether it is derived from the piperylene singlet or triplet states is impossible to say at this time.

H. 1-Phenyl-2-butene-Sensitized Isomerization of *cis*-Piperylene. This experiment was run in order to determine how much, if any, triplet energy transfer from phenylbutene to piperylene occurred in solution. Correction was made for the fraction of light absorbed by the diene at 254 nm and the resultant contribution to the overall isomerization from isomerization due to direct irradiation (see **G**). *trans*-1-Phenyl-2-butene was found to sensitize the cis → trans isomerization of piperylene with a quantum efficiency of 0.005. When correction is made for the decay ratio of piperylene triplets,[20] the quantum efficiency of piperylene triplet formation is found to be 0.009 (it is assumed that none of the isomerization arises from the singlet quenching act (see Discussion)).

Discussion

A. Fluorescence Quenching. Although the quenching of benzene and toluene fluorescence by olefins has been studied in the gas phase,[24–26] no comparable study has been reported for such quenching of these molecules in solution.[27,28] *The data presented herein show clearly that such quenching cannot only occur but is highly efficient.* Some of the pertinent rate data are gathered in Table V; they have been calculated from the slopes of the quenching curve with the assumption that oxygen quenches the fluorescence of benzenoid aromatics at a diffusion-controlled rate.[8,29] Since the oxygen data are based on only one point, and the concentration of the oxygen during that measurement can only be estimated, the absolute values presented here are of import mainly as an indication of the rapidity of the quenching act and of the relative efficiency of dienes *vs.* monoolefins. The only solution phase data useful for purposes of comparison are those published for the quenching of the naphthalene singlet state. The estimated rate constants for *cis*-piperylene in the phenyl systems are *ca.* 70 times the value (9.2 × 10^7) reported for naphthalene[4a] and, in fact, are in the same range as the diffusion-controlled rate constants observed for triplet energy transfer. Furthermore, whereas cyclohexene is 5% as efficient a quencher of naphthalene singlets as piperylene,[30] the 2-hexenes are 500 times less efficient than piperylene with benzenoid aromatics.

Table V. Rate Constants for Singlet Quenching of *trans*-1-Phenyl-2-butene and Toluene

Quencher	Rate constant (k_q) × 10^7 M^{-1} sec^{-1}
Toluene	
Oxygen	1590
cis-Piperylene	800
trans-2-Hexene	1.5
trans-1-Phenyl-2-butene	
Oxygen	1590
cis-Piperylene	465
cis-2-Hexene	1.2
trans-2-Hexene	0.62

Our observation that negligible piperylene isomerization results from irradiation of phenylbutene–piperylene mixtures (*cf.* Results, section **H**) supports the postulate that enhanced radiationless decay[4a] and not electronic energy transfer[31] is a consequence of the quenching act (direct irradiation of piperylene leads to significant isomerization; *cf.* Results, section **G**).

B. Toluene–Heptene Intermolecular Triplet Energy Transfer. The sensitized cis–trans isomerization of olefins by an aryl triplet donor can be described by eq 1–8.[19] D, ^{1}D, and ^{3}D represent the aryl donor in its

$$\mathrm{D} + h\nu \longrightarrow {}^1\mathrm{D} \tag{1}$$

$$ {}^1\mathrm{D} \longrightarrow \mathrm{D}\ (+h\nu) \tag{2}$$

$$ {}^1\mathrm{D} \longrightarrow {}^3\mathrm{D} \tag{3}$$

$$ {}^3\mathrm{D} \longrightarrow \mathrm{D} \tag{4}$$

$$ {}^3\mathrm{D} + \mathrm{O_t} \longrightarrow \mathrm{D} + {}^3\mathrm{X} \tag{5}$$

$$ {}^3\mathrm{D} + \mathrm{O_c} \longrightarrow \mathrm{D} + {}^3\mathrm{X} \tag{6}$$

$$ {}^3\mathrm{X} \longrightarrow \mathrm{O_t} \tag{7}$$

$$ {}^3\mathrm{X} \longrightarrow \mathrm{O_c} \tag{8}$$

ground, excited singlet, and excited triplet states, O_c and O_t represent the *cis*- and *trans*-olefin, and ^{3}X represents a twisted[19,32,33] olefin triplet species. Equation 2

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cis-piperylene. We have now measured this extinction coefficient in our own laboratory as 15.

(18) N. J. Turro, Ph.D. Thesis, California Institute of Technology, 1965.

(19) G. S. Hammond, *J. Amer. Chem. Soc.*, **86**, 3197 (1964).

(20) A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, **43**, 2129 (1965).

(21) S. Boue and R. Srinivasan, *J. Amer. Chem. Soc.*, **92**, 3226 (1970); J. Saltiel, J. Metts, and M. Wrighton, *ibid.*, **92**, 3227 (1970).

(22) Some of the data were determined by W. Ferree, Jr., in these laboratories.

(23) We are grateful to R. Brainard of this laboratory for this determination.

(24) E. K. C. Lee, H. O. Denschlag, and G. A. Haninger, Jr., *J. Chem. Phys.*, **48**, 4547 (1968).

(25) A. Morikawa and R. J. Cvetanovic, *ibid.*, **49**, 1214 (1968).

(26) E. K. C. Lee, M. W. Schmidt, G. R. Shortridge, Jr., and G. A. Haninger, Jr., *J. Phys. Chem.*, **73**, 1805 (1969).

(27) Internal quenching of the phenyl singlet state by olefins has been observed; see (a) H. Morrison and W. I. Ferree, Jr., *Chem. Commun.*, 269 (1969). See also (b) G. R. Ziegler, *J. Amer. Chem. Soc.*, **91**, 446 (1969), and (c) J. R. Edman, Abstracts, 157th National Meeting of the American Chemical Society, April 14–18, 1968, Minneapolis, Minn., No. ORGN 140.

(28) Fluorescence quenching of benzene by olefins in solution has also been observed by Wilzbach and Kaplan (private communication).

(29) (a) E. J. Bowen, *Chem. Brit.*, **2**, 249 (1964); (b) C. S. Burton and W. A. Noyes, Jr., *J. Chem. Phys.*, **49**, 1705 (1968).

(30) S. L. Murov, R. S. Cole, and G. S. Hammond, *J. Amer. Chem. Soc.*, **90**, 2957 (1968).

(31) F. S. Wettack, *J. Phys. Chem.*, **73**, 1167 (1969).

(32) R. S. Mullikan and C. C. J. Roothaan, *Chem. Rev.*, **41**, 219 (1947); A. J. Merer and R. S. Mullikan, *ibid.*, **69**, 639 (1969).

(33) Z. R. Grabowski and A. Bylina, *Trans. Faraday Soc.*, **60**, 1131 (1964).

summarizes both radiationless and radiative unimolecular singlet decay; singlet quenching has been omitted since less than 1% of toluene's fluorescence is quenched by *trans*-2-hexene at a concentration (2×10^{-2} *M*) sufficient to eliminate completely toluene phosphorescence. A kinetic analysis of eq 1–8 leads to the following expressions for quantum efficiencies of isomerization of pure trans or cis isomers (eq 9 and 10). The three terms on the right side of the

$$\phi_{t\rightarrow c} = \frac{k_3}{k_2 + k_3}\,\frac{k_5[O_t]}{k_4 + k_5[O_t]}\,\frac{k_8}{k_7 + k_8} \tag{9}$$

$$\phi_{c\rightarrow t} = \frac{k_3}{k_2 + k_3}\,\frac{k_6[O_c]}{k_4 + k_6[O_c]}\,\frac{k_7}{k_7 + k_8} \tag{10}$$

equations represent efficiencies of intersystem crossing, energy transfer, and decay with isomerization (decay ratio), respectively. The ratio of the quantum yields is given by

$$\frac{\phi_{t\rightarrow c}}{\phi_{c\rightarrow t}} = \frac{k_8}{k_7}\,\frac{k_5[O_t]}{k_6[O_c]}\,\frac{k_4 + k_6[O_c]}{k_4 + k_5[O_t]} \tag{11}$$

The photostationary state is given by

$$[O_c]_{pss}/[O_t]_{pss} = (k_5/k_6)(k_8/k_7) \tag{12}$$

When $[O_t] = [O_c]$, eq 11 transforms into

$$\frac{\phi_{t\rightarrow c}}{\phi_{c\rightarrow t}} = \frac{[O_c]_{pss}}{[O_t]_{pss}}\,\frac{k_4 + k_6[O_c]}{k_4 + k_5[O_t]} \tag{13}$$

Whereas a considerable number of studies have been made of the benzene[24,34–41] and toluene[29b,35b,41b] sensitized isomerization of aliphatic monoolefins in the gas phase, relatively few reports have appeared which deal with these reactions in solution.[16,35e,42–44] It has been shown[24] that for benzene triplet energy transfer to olefins in the gas phase, $k_5 = k_6 = 2 \times 10^9$ M^{-1} sec^{-1}. The rate constant for decay (k_4) has been assigned a value (8×10^4 sec^{-1}) which would make it noncompetitive with the energy transfer step.[35c] Under these circumstances, eq 13 simplifies to eq 14, and a test of the

$$\phi_{t\rightarrow t}/\phi_{c\rightarrow t} = [O_c]_{pss}/[O_t]_{pss} \tag{14}$$

mechanism is easily performed. In fact, the photostationary state for benzene-sensitized isomerization of 2-butene in the gas phase is 1.0–1.09, while the ratio of quantum efficiencies is 0.98[24,38a] and the data are thus in good agreement with eq 14. However, the available data for benzene sensitization in solution are limited and ambiguous. The photostationary states for isomerization of several aliphatic olefins is 1.0,[16] but the only quantum efficiencies reported for a pair of trans–cis isomers are those for 2-butene. The data[15] are $\phi_{t\rightarrow c} \cong 0.03$ and $\phi_{c\rightarrow t} \cong 0.04$ with a resultant ratio of 0.75. Since the experimental error involved in these latter determinations is not reported, it is impossible to say whether the apparent failure of eq 14 is real (we have confirmed that the photostationary state with 2-heptene as acceptor is 1.0).

Whatever the case may be for benzene, we now have data which indicate that for the toluene–2-heptene system in solution, the simplified relationship of eq 14 is definitely invalid. The photostationary state $[O_c]/[O_t]$ is 0.74 ± 0.01 whereas the ratio of quantum efficiencies ($\phi_{t\rightarrow c}/\phi_{c\rightarrow t}$) is 1.15 ± 0.15. These data must then be related by the more rigorous expression, eq 13. A rigorous study of the dependence of ϕ on heptene concentration has not been made; however, a consideration of the data available (*cf.* Table II) suggests that at the heptene concentrations used in these experiments, ϕ is independent of olefin concentration and thus $k_4 \ll k_5[O_t]$ and $k_6[O_c]$. Since the quantum efficiencies were determined at identical olefin concentrations, eq 1 reduces to eq 15 and eq 13 to eq 16. The "excitation

$$\frac{\phi_{t\rightarrow c}}{\phi_{c\rightarrow t}} = \frac{k_8}{k_7} \tag{15}$$

$$\frac{\phi_{t\rightarrow c}}{\phi_{c\rightarrow t}} = \frac{[O_c]_{pss}\,k_6}{[O_t]_{pss}\,k_5} \tag{16}$$

ratio," k_6/k_5, is thus 1.55 (the cis isomer is a better triplet acceptor than the trans) while the decay ratio, $k_8/k_7 = 1.15 \pm 0.15$.

The deviation of the excitation ratio from unity may be a consequence of the lowered (83 kcal)[45] triplet energy of toluene relative to benzene (84 kcal)[45] since a triplet energy for ethylene has been placed[46] at 82 kcal (the 2-butene grouping is presumably slightly lower[47]). Because of the experimental errors involved in the quantum efficiency ratio, it is difficult to ascertain whether the apparent deviation of the decay ratio from unity is, in this case, significant[48] (see, however, the 1-phenyl-2-butene discussion below).

C. Intramolecular Interactions in the 1-Phenyl-2-butene Molecule. We have elsewhere proposed[3] a mechanism for the photoisomerization of 1-phenyl-2-butene which is the intramolecular equivalent of eq 1–8. This requires that the aryl olefin be viewed as a composite molecule in which phenyl and olefin chromophores are, to a first approximation, noninteracting. Thus, the ultraviolet absorption spectrum of 1-phenyl-2-butene is similar to (though not identical with) that of toluene in the region accessible by common instrumentation (*e.g.*, $\lambda > 220$ nm).[49] This would suggest that ground-state interactions are minor. We would expect that interaction in the excited singlet state would

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Table VI. Quantum Yields and Kinetic Data for the Photophysical Processes of the Excited Singlet States of *trans*-1-Phenyl-2-butene and Toluene

ϕ_f	ϕ_{ic}	ϕ_d	$\tau \times 10^{-8}$ sec	$k_f \times 10^6$ sec^{-1}	$k_f' \times 10^6$ sec^{-1}	$k_d \times 10^7$ sec^{-1}	$k_{ic} \times 10^7$ sec^{-1}
			trans-1-Phenyl-2-butene				
0.08	0.36	0.56	2.7	3.0	2.8	2.1	1.4
			Toluene				
	0.30	0.60	2.0	5.0	2.6	3.0	1.5
0.10^a	0.25^a 0.29^b	0.65^a	3.0^a	3.31^a		2.15^a	0.83^a

^{a} *Cf.* ref 10. ^{b} *Cf.* ref 15.

manifest itself in a perturbation of the fluorescence spectrum, either in position or intensity. Such perturbations have been found in other systems whereby extensive internal fluorescence quenching is observed.[1,27,50] For example, the relative fluorescence efficiencies of toluene, 1-phenylhexane, and 6-phenyl-2-hexene[12] are 1.00:0.84:0.05. On the other hand, 1-phenyl-2-butene has a value of 0.79 relative to toluene, virtually identical with the 0.82 observed for 1-phenylbutane.

A more complete comparison of the singlet state properties of toluene and 1-phenyl-2-butene is available from the data in Table VI. In Table VI, ϕ_f, ϕ_{ic}, and ϕ_d represent the quantum efficiencies for fluorescence, intersystem crossing, and decay with the associated rate constants labeled in like fashion (k_f and k_f' are the same rate constant calculated by two different methods, see below). τ is the measured lifetime of the singlet state. ϕ_f for 1-phenyl-2-butene was calculated from its fluorescence efficiency relative to toluene. ϕ_{ic} for this substrate is the sum of the quantum efficiencies for trans $\rightleftarrows$ cis isomerization and is a minimum value; if energy transfer is less than 100% efficient, ϕ_{ic} will increase accordingly. ϕ_{ic} for toluene is calculated from the sensitized isomerization quantum efficiencies. ϕ_d is $1 - (\phi_f + \phi_{ic})$. τ has been calculated from our oxygen quenching data by the method of Berlman[8] (*i.e.*, $\phi_0/\phi = 1 + k_q\tau[O_2]$) using a value for k_q of $1.5 \times 10^{10}\ M^{-1}$ sec^{-1} and the concentration of oxygen as $2 \times 10^{-3}\ M$. The rate constants of fluorescence are $k_f = \phi_f/\tau$ and $k_f' = \epsilon_{max}/10^{-4}$. The other constants, k_d and k_{ic}, were calculated using $k_d = k_f\phi_d/\phi_f$ and $k_{ic} = k_f\phi_{ic}/\phi_f$.

The properties we observe for the singlet state of toluene agree well with what has been reported in the literature. Furthermore, the data for 1-phenyl-2-butene show a good correlation with those for toluene. *This agreement lends support to our postulate that the aromatic moiety in 1-phenyl-2-butene is not appreciably perturbed in its excited singlet state by the presence of the nonconjugated olefin group.*

By contrast with what is observed for fluorescence emission, no phosphorescence from highly purified samples of 1-phenyl-2-butene could be detected. Luminescence experiments involving toluene–piperylene mixtures in viscous ethanol glasses provide confirmation that this lack of emission is *not* a result of intermolecular quenching and support our hypothesis that internal triplet energy transfer takes place. Similar conclusions have been reached by others for gas-phase photolysis of 1-phenyl-2-butene.[51]

As mentioned above, internal sensitization may be viewed as the intramolecular analog of eq 1–8, whereby the photostationary state is shown in eq 17 and the quantum efficiency ratio in eq 18. In these equations, ϵ_t and ϵ_c represent the molar extinction coefficients of the two isomers at 254 nm while $\phi_{et(t)}$ and $\phi_{et(c)}$ are the quantum efficiencies for internal energy transfer. If one assumes internal transfer to be 100% efficient (*i.e.*, that $k_4 \ll k_5$ (k_5 and k_6 now being first-order rate constants)), then the decay ratio, k_8/k_7, should be equal to the ratio of quantum efficiencies and to the photostationary state value divided by the extinction coefficient ratio (eq 19). The quantum efficiency ratio is 1.25; the

$$\frac{[O_c]_{pss}}{[O_t]_{pss}} = \frac{\epsilon_t\,\phi_{et(t)}\,k_8}{\epsilon_c\,\phi_{et(c)}\,k_7} \tag{17}$$

$$\frac{\phi_{t\to c}}{\phi_{c\to t}} = \frac{\phi_{et(t)}\,k_8}{\phi_{et(c)}\,k_7} \tag{18}$$

$$\frac{k_8}{k_7} = \frac{\phi_{t\to c}}{\phi_{c\to t}} = \frac{[O_c]_{pss}\,\epsilon_c}{[O_t]_{pss}\,\epsilon_t} \tag{19}$$

photostationary (1.19) times the extinction coefficient ratio (1.02) is 1.21. We have previously noted[3] the agreement between these values as evidence in favor of the mechanistic scheme. The decay ratio (av 1.23) is in satisfactory agreement with the value of 1.15 observed with toluene.

The rate constant for intramolecular energy transfer had previously[3] been calculated using piperylene quenching data. Since this quenching is now known to be of the singlet state an alternate approach was used. Irradiation of 1-phenyl-2-butene in the presence of 0.018 *M* *cis*-piperylene led to diene isomerization with a quantum efficiency of 5×10^{-3} (after correction for isomerization by light absorbed by the diene). This corresponds to a quantum efficiency of piperylene triplet formation of 9×10^{-3} (division by 0.55 is necessary to correct for the decay ratio[20]). Now, the intersystem crossing efficiency of 1-phenyl-2-butene is taken to be a minimum of 0.36 but, since ϕ_0/ϕ for quenching of the singlet by 0.018 *M* piperylene is *ca.* 3, the ϕ_{ic} of phenylbutene under the conditions of this experiment may be reduced to *ca.* 0.12. Thus, only 0.009/0.12 or 7.5% of available aryl triplets are transferring their energy to piperylene. If the rate constant for external transfer is diffusion controlled ($1.5 \times 10^{10}\ M^{-1}$ sec^{-1}), the pseudo-

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first-order rate constant for such transfer is $k_q[Q]$ or 2.7×10^8 sec^{-1}. For such a rate to give only 7.5% external transfer, *intramolecular energy transfer must have a first-order constant of* $2.7 \times 10^8/7.5 \times 10^{-2}$ *or* $\geq 3.6 \times 10^9$ *sec*$^{-1}$.[52]

Finally, some anomalies in the comparative quenching efficiencies for 1-phenyl-2-butene fluorescence *vs.* photoisomerization warrant mention. Whereas *cis*-piperylene quenches *trans*-1-phenyl-2-butene fluorescence with a Stern–Volmer efficiency of 120.4 M^{-1}, the quenching of t → c isomerization is only 65.0 M^{-1}. It is tempting to discount the obvious discrepancies between these numbers as a consequence of experimental error, especially with their large dependence on oxygen concentration (*cf.* Table I). However, the value for quenching cis → trans isomerization (60.9 M^{-1}) correlates well with the chemical quenching cited above, and more recent studies of fluorescence quenching with a different spectrometer indicate that, if anything, the 120.4 figure is slightly low.[53] Furthermore, similar variations in fluorescence *vs.* chemical quenching have been observed for the 1-phenyl-1-butene[54] and 6-phenyl-2-hexene[12] systems.

The obvious conclusion would be that (nonquenchable) upper vibrational states contribute to the photoisomerization, and quantum efficiency *vs.* excitation wavelength studies in the 6-phenyl-2-hexene system confirm this view for that system.[12] However, 1-phenyl-2-butene photoisomerization *decreases* with increasing frequency of irradiation (as does the 1-phenyl-1-butene isomerization[54]) and the simple rationale does not, therefore, suffice. A comparable anomaly has been experienced with intersystem crossing *vs.* fluorescence quenching in the phenylacetic ester system[55] and further investigations in this area are in progress.

Experimental Section

Materials. *cis*-1,3-Pentadiene (Chem. Samples), *trans*-2-hexene (Chem. Samples and Aldrich), and *trans*-2-heptene (Chem. Samples) were distilled immediately before use in a micro-distillation apparatus.[56] *cis*-2-Hexene (Chem. Samples) and *cis*-2-heptene (K & K Labs) were purified by preparative glpc, using a 10 ft × 3/8 in. 30% $AgNO_3$-ethylene glycol column, and were distilled immediately before use. *trans*- and *cis*-1-phenyl-2-butene were obtained by the reported procedure.[2,3] Toluene ("Baker Analyzed" reagent grade), benzene (Mallinckrodt spectrophotometric grade), and spectral grade cyclopentane (Phillips, Matheson Coleman and Bell, and Burdick and Jackson) were used as received. Isopentane (Phillips) was purified by passing the solvent through two silica gel chromatography columns. Absolute ethanol was obtained by the method of Lund and Bjerrum[57] and stored under nitrogen.

Instrumentation. Analyses for *cis*- and *trans*-1-phenyl-2-butene were carried out by the reported procedure.[3] Analyses for *cis*- and *trans*-2-heptene were performed using a 20 ft × 0.25 in. β,β'-oxydipropionitrile column at 0° in a Varian-Aerograph 90-P3 chromatograph with accompanying Leeds and Northrup recorder and attached Disc integrator. Cyclohexane was employed as an internal standard for the heptene analyses. Fluorescence and phosphorescence spectra were determined with an Aminco-Bowman spectrophotofluorometer employing a 150-W xenon arc for excitation and either a RCA 1P28 or a EMI 9558QA photomultiplier tube for detection. The 1P28 system was calibrated employing rhodamine B and sodium 1-dimethylaminonaphthalene-5-sulfonate quantum counters.[58,59] Later spectra were recorded on a more sensitive homemade instrument described in detail elsewhere.[55]

Quantum Yields for the Toluene-Sensitized Isomerization of 2-Heptene. Varying amounts of toluene (9.4×10^{-2} to 25 g, 1.02×10^{-3} to 2.7×10^{-1} mol) and cyclopentane were made up to a total volume of 50 ml in Vycor tubes and deaerated by bubbling with argon. *trans*- or *cis*-2-heptene (490 mg, 5×10^{-3} mol) was added to each tube; the samples were irradiated in a turntable apparatus using a Hanovia low-pressure mercury resonance lamp.[3] All quantum yields were corrected for slight back-reaction. A small loss of 2-heptene was observed which amounted to no more than 2% of the original starting material. The light intensity was determined during photolysis by uranyl oxalate actinometry.

Photostationary State for the 2-Heptene Isomerization Sensitized by Toluene. To 100 ml of cyclopentane, contained in a water-jacketed cylindrical Pyrex vessel,[3] were added toluene (10 ml, 9.4×10^{-2} mol) and 2-heptene (1.35 ml, 1.1×10^{-2} mol) of varying isomer composition. The solution was deaerated by bubbling with argon and irradiated using the low-pressure mercury lamp. After a photostationary state was obtained, as determined by periodic analysis of aliquots, the solution was analyzed and the ratio of the two isomers obtained.

Isomerization Quenching Experiments. The quenching of the isomerization of either *trans*- or *cis*-1-phenyl-2-butene was carried out by the previously reported procedure.[3]

Fluorescence and Phosphorescence. The fluorescence spectra of 1-phenyl-2-butene and toluene were determined in cyclopentane solution at 25°. In the spectra determined using the 150-W xenon lamp for excitation, the excitation monochromator was set to give 254-nm light. In some determinations excitation was achieved by direct irradiation of the sample using a mercury pen lamp emitting principally at 253.7 nm. All solutions were thoroughly deaerated by bubbling with argon. The concentration of the substrate (1-phenyl-2-butene or toluene) varied between 3×10^{-3} and 5×10^{-3} M. Phosphorescence spectra were determined in both isopentane and ethanol glasses in a micro-quartz tube (American Instrument Co.) placed in a small dewar flask containing liquid nitrogen. The room temperature concentrations of the substrates were between 2×10^{-2} and 3×10^{-2} M. All phosphorescence samples were degassed, by five freeze–thaw cycles at a minimum pressure of 2×10^{-2} mm, and then sealed. Comparative quantum efficiency data were obtained with solutions of equal absorbance.

Fluorescence Quenching Experiments. To solutions of *trans*- or *cis*-1-phenyl-2-butene (27 mg, 2.1×10^{-4} mol) or toluene (23 mg, 2.4×10^{-4} mol) in 50 ml of cyclopentane were added varying amounts of *trans*- or *cis*-2-hexene (0.79 to 3.7 g, 9.4×10^{-3} to 4.2×10^{-2} mol) or *cis*-1,3-pentadiene (9–63 mg, 1.3×10^{-4} to 9.3×10^{-4} mol). The solutions were deaerated by bubbling with argon. In the *cis*-1,3-pentadiene experiments correction was made for the light absorbed by the diene. In the oxygen quenching experiments the solutions of the substrates were bubbled with a fast stream of air. The resulting oxygen concentration was estimated to be 2×10^{-3} M.[11]

1-Phenyl-2-butene Photosensitized Isomerization of *cis*-Piperylene. A solution of 1-phenyl-2-butene (133 mg, 1.0 mmol), *cis*-piperylene (60 mg, 0.88 mmol), and cyclopentane (50 ml) was deaerated with argon and irradiated in a Vycor tube with the low pressure mercury lamp for 1.5 hr. The *trans*-piperylene formed was measured by vpc using the β,β'-oxydipropionitrile column at 0°; conversions of 2.1 and 2.3% were observed by two analyses of the reaction mixture. The incident light intensity was 1.9×10^{17} quanta/sec so that the $\phi_{c\rightarrow t}$ for piperylene was 0.0103. After correction for light absorption by the diene (6%) and the quantum efficiency for direct isomerization (0.087), the calculated sensitized $\phi_{c\rightarrow t}$ is 0.005.

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[52] This number represents a minimum value; to the extent that any part of the observed piperylene isomerization was caused by other than phenylbutene triplet sensitization, the rate contant for *internal* transfer is correspondingly higher than this estimate. A value of 2×10^6 sec^{-1} was recently assigned[13] on the basis of a reported concentration dependence for the quantum efficiency of isomerization. Such a dependence is not obvious from our data, and this low a value seems inconsistent with the inability of 1-phenyl-2-butene to sensitize piperylene isomerization.

[53] In the same vein, though oxygen quenches phenylbutene fluorescence, it has no apparent effect on isomerization efficiency. Comtet[51] has observed the same phenomenon in the gas phase. This may be due to a quenching of the singlet state *via* enhanced intersystem crossing[12] (*cf.* C. S. Parameter and J. D. Rau, *J. Chem. Phys.*, 51, 2242 (1969)), but this explanation requires a difficult-to-accept coincidence of competing effects.

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Table VII. Photoisomerization of *trans*-1-Phenyl-2-butene as a Function of Wavelength

λ, nm	*trans*-II, mg	Time, hr	Intensity × $10^{14\,a}$	*cis*-II Obsd	*cis*-II Corr[b]	Convn,[c] %	ϕ
246[d]	179.6	48	3.82	1.6	1.6	0.9	0.13
			2.70				
			Av 3.26				
254[e]							0.20
262	179.6	48	10.58	8.8	9.2	4.9	0.25
			8.79				
			Av 9.68				

[a] Photons/second. [b] Corrected for back-reaction. [c] Uncorrected. [d] The actual values are 246 ± 11 and 262 ± 11 nm. [e] This is the value from irradiation with the 2537-Å lamp, and is given here for comparison only.

Photoisomerization of *cis*-Piperylene. These experiments were conducted in a manner identical with the one above but in the absence of any sensitizer (the piperylene was purified immediately prior to use and the solvent was transparent in the uv). Conversions of *cis*- to *trans*-piperylene were 2–9%. Because all the incident 254-nm light is not absorbed under these conditions, the effective path length of the Vycor tubes was determined by actinometry using low concentrations of 6-phenyl-2-hexene and independently measured quantum efficiencies of product formation.[12] Although the tubes are 25 mm o.d., the effective path length was measured as 13.5 mm. This value was used to calculate the absorbance of the piperylene solutions and the ϕ's observed were 0.083, 0.086, and 0.094; av 0.087.

Photoisomerization of *trans*-1-Phenyl-2-butene as a Function of Concentration. Two 50-ml solutions of *trans*-1-phenyl-2-butene, 7.07×10^{-3} *M* (46.8 mg) and 2.55×10^{-2} *M* (168.8 mg), were prepared with spectral grade *n*-hexane. The *trans*-1-phenyl-2-butene was weighed into the Vycor tubes and the solutions were deoxygenated with argon 1 hr prior to irradiation with 2537 Å light in the turntable at 25.0 ± 1.0°. The standard was added, and the tubes were analyzed for *cis*-1-phenyl-2-butene on a 4% $AgBF_4$–16% Carbowax 20M column. The 7.07×10^{-3} *M* solution was photolyzed 32 min with a lamp intensity of 1.11×10^{17} photons/sec. Before correction for back-reaction, 7.7 mg (16.4%) of *cis*-1-phenyl-2-butene was detected; after correction the value became 9.1 mg, $\Phi = 0.195$. The 2.55×10^{-2} *M* solution was irradiated 41 min with 2537 Å light (1.11×10^{17} photons/sec). The 12.1 mg (7.7%) of *cis*-1-phenyl-2-butene measured by glpc was corrected for back-reaction, and the corrected value of 13.0 mg was obtained, $\phi = 0.218$.

Photoisomerization of *trans*-1-Phenyl-2-butene as a Function of Wavelength. The quantum efficiency of isomerization of *trans*-1-phenyl-2-butene at 246 ± 11 nm and 262 ± nm was examined. An 80-ml sample of 1.69×10^{-2} *M* *trans*-1-phenyl-2-butene in spectral grade *n*-hexane was cooled to 18–20° in a 6.6-cm path length water-jacketed cell, and the solution was deoxygenated with argon for 1 hr. A Bausch and Lomb "high intensity monochromator" was used to resolve the emission from the mercury–xenon lamp. Slit widths of 6.0 mm and 3.4 mm were used to obtain the maximum intensity. The optical density of the solutions was 2.0 over the entire band pass. Chemical actinometry was used to measure the lamp intensity before and after each experiment and then averaged. The results and conditions are summarized in Table VII.

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Dual Reaction Pathways in an Open-Chain Cope Rearrangement

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Abstract: *meso*-3,4-Diphenylhexa-1,5-diene rearranges with a half-life of about 15 hr at 120° to *cis,trans*-1,6-diphenylhexa-1,5-diene (63%) and *trans,trans*-1,6-diphenylhexa-1,5-diene (37%). The cis,trans isomer is formed through a transition state having four-center, chairlike geometry whereas the trans,trans isomer requires a six-center, boatlike transition state. The corresponding *dl*-3,4-diphenylhexa-1,5-diene is converted with a half-life of about 8 hr at 80° to 100% of the trans,trans isomer, a product which requires a four-center transition state. The "preferred" geometry for thermal Cope rearrangements is four centered, based on the known rearrangement stereochemistry of *meso*- and *dl*-3,4-dimethylhexa-1,5-diene. The exceptional behavior of the *meso*-diphenyl derivative appears to be a consequence of steric inhibition to coplanarity of contiguous phenyl and allyl groups in the four-center transition state derived from this molecule.

Transition-state geometries for the thermal Cope rearrangement[3] can generally be classified as either of two basic types—four-center, chairlike or six-center, boatlike. An example of the former is provided by the rearrangement of *meso*-3,4-dimethylhexa-1,5-diene (**1a**) at 225° to *cis,trans*-octa-2,6-diene (**3a**) as the virtually exclusive product (99.7%).[4] Of the two transition-state geometries, the four-center (**2a**) as shown accounts

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(1) To whom inquiries should be directed at Portland State University. Some of the preliminary experimental work was carried out at Harvard University, Cambridge, Mass.

(2) National Science Foundation Undergraduate Research Participant.

(3) The traditional definition of the Cope rearrangement is assumed. For reviews, see (a) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," 2nd ed, Cornell University Press, Ithaca, N. Y., 1969, pp 867–869, and (b) S. J. Rhoads in "Molecular Rearrangements," P. de Mayo, Ed., Vol. 1, Interscience, New York, N. Y., 1963, Chapter 11.

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