Photochemistry of Bichromophoric Molecules. Intramolecular Cycloaddition and Cis–Trans Isomerization of 6-Phenyl-2-hexene in Solution[1,2]

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Abstract: The photochemical and photophysical properties of the title compound have been studied in solution, in order to ascertain in what ways the two functional groups of this bichromophoric molecule might interact upon excitation of the benzene ring. The major photoprocesses are internal cycloaddition of the double bond to the benzene ring, and cis–trans isomerization about the double bond. The cycloadducts formed are 7-*exo*-methyl-6-*endo*-*H*-tetracyclo[6.2.1.0.^{2,11}0.^{2,6}]-9-undecene (IIa) and 3-*exo*-methyl-4-*endo*-*H*-tetracyclo[6.2.1.0.^{2,11}0.^{4,8}]-9-undecene (IIb) from *cis*-6-phenyl-2-hexene and 3-*endo*-methyltetracyclo[3.2.1.0.^{2,8}3.^{4,8}]-6-undecene (III) from *trans*-6-phenyl-2-hexene. Quantum efficiencies are 0.26 for cycloaddition of the *cis*-phenylhexene and 0.011 for cis → trans isomerization. Whereas the absorption spectrum of 6-phenyl-2-hexene is unexceptional, the fluorescence emission (though toluene-like in location and appearance) is much reduced in intensity and no phosphorescence is observable. The singlet lifetime is likewise found to be considerably shortened. Cycloaddition is quenched less efficiently than is fluorescence and the quantum efficiency for this photoreaction is found to increase markedly with increasing excitation energy. It is proposed that cycloaddition originates from an aryl olefin exciplex, formed upon excitation of the aryl ring; the rapid formation of this exciplex is responsible for the diminished singlet (monomer) lifetime and fluorescence. Olefin isomerization probably arises from intramolecular triplet–triplet energy transfer (oxygen is found to *enhance* the efficiency of isomerization), with the small quantum yield primarily a result of much diminished aryl intersystem crossing. It is suggested that such greatly reduced intersystem crossing may be a general consequence of rapid interaction between two nonconjugated chromophores in bichromophoric molecules.

As part of an ongoing program concerned with the photochemistry of nonconjugated, bichromophoric molecules[1,4,5] we studied in some detail the solution phase cis–trans photoisomerization of 1-phenyl-2-butene.[1,4b,c,e] Our results have led us to propose[1,4c,e] that olefin isomerization in this system is a consequence of intramolecular triplet energy transfer with the aryl chromophore acting as the donor. As a first step toward determining the structural requirements for such transfer, we decided to examine 6-phenyl-2-hexene in order to ascertain what, if any, effect would result from an elongation of the (flexible) carbon chain insulating the phenyl and olefin moieties.[6]

Results

A. Preparation of the Isomeric 6-Phenyl-2-hexenes *cis*-6-Phenyl-2-hexene (*cis*-I) was prepared by hydrogenation of 6-phenyl-2-hexyne over poisoned palladium and contained 1.1–1.2% *trans*-6-phenyl-2-hexene (*trans*-I) as the only impurity. The mass spectrum has a parent peak of *m/e* 160 and the elemental analysis fits $C_{12}H_{16}$. The nmr spectrum verifies the presence of two vinyl protons, five aryl protons, a methyl doublet (with splitting of 5 Hz assigned to coupling to the adjacent vinyl proton with additional broadening due to long-range coupling to the second vinyl proton), a methylene triplet (J = 7 Hz) assigned to the benzylic protons, and four other aliphatic protons.

A mixture containing 70% *trans*-I was prepared by the Grignard coupling of β-phenylethylmagnesium bromide with crotyl bromide, and the purity increased to 99% or higher by chromatography on $AgNO_3$-impregnated silica gel. The elemental analysis fits $C_{12}H_{16}$. The nmr spectrum is similar to that of *cis*-I except that the methyl resonance now appears as four lines (J = 2.5 and 1 Hz), reflecting observable coupling to the nonadjacent vinyl proton as well as the adjacent one, as expected for a trans geometry, and the vinyl pattern is different. The ir spectrum is identical with that of *cis*-I except that a strong band appears at 10.37 μ, typical of the trans-substituted double bond. The uv spectra of *cis*-I and *trans*-I are approximately identical with that of toluene.

B. Photolysis of *cis*-I. Irradiation of a 0.6 *M* solution of *cis*-I in cyclopentane using 254-nm light resulted in efficient conversion to a mixture of isomers, II, together with a minor (as yet unidentified) product. In addition, photolyses carried to relatively small conversions demonstrated that cis → trans isomerization of I was also occurring but with an efficiency much

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[1] Organic Photochemistry. XV. Part XIV: H. Morrison, J. Pajak, and R. Peiffer, *J. Amer. Chem. Soc.*, **93**, 3978 (1971).

[2] Abstracted from the doctoral dissertation of William Ferree, Jr., Purdue University, Jan 1971. Presented, in part, at the 160th National Meeting of the American Chemical Society, Chicago, Ill., Sept 13–18, 1970.

[3] Author to whom inquiries concerning this paper should be addressed.

[4] (a) H. Morrison, *Tetrahedron Lett.*, 3653 (1964); (b) H. Morrison, *J. Amer. Chem. Soc.*, 87, 932 (1965); (c) H. Morrison, R. Brainard, R. Peiffer, and D. Richardson, Abstracts, 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 10–14, 1967; (d) H. Morrison, R. Brainard, and D. Richardson, *Chem. Commun.*, 1653 (1968); (e) H. Morrison and R. Peiffer, *J. Amer. Chem. Soc.*, 90, 3428 (1968); (f) H. Morrison and W. I. Ferree, Jr., *Chem. Commun.*, 268 (1969); (g) H. Morrison and S. R. Kurowsky, Abstracts, 157th National Meeting of the American Chemical Society, Minneapolis, Minn., April 14–18, 1969; (h) R. Brainard and H. Morrison, *J. Amer. Chem. Soc.*, **93**, 2685 (1971); (i) H. Morrison and S. R. Kurowsky, *ibid.*, in press.

[5] The rapidly increasing activity in this area, which has recently become evident, is exemplified by these most recent publications: (a) N. W. Tyer, Jr., and R. S. Becker, *ibid.*, **92**, 1295 (1970); (b) D. O. Cowan and A. A. Baum, *ibid.*, **92**, 2153 (1970); (c) R. S. Cooke and G. S. Hammond, *ibid.*, **92**, 2739 (1970); (d) E. C. Sanford and G. S. Hammond, *ibid.*, **92**, 3497 (1970); (e) M. Comtet, *ibid.*, **92**, 5308 (1970); (f) O. Yonemitsu, Y. Okuno, Y. Kanoaka, and B. Witkop, *ibid.*, **92**, 5686 (1970).

[6] See ref 4f for a preliminary communication of this study.

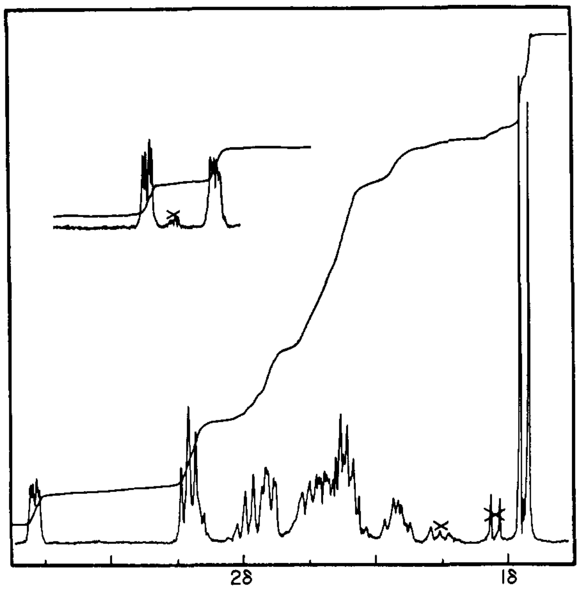

Figure 1. 220-MHz spectrum of IIa in carbon tetrachloride. Peaks marked with X are due to impurities.

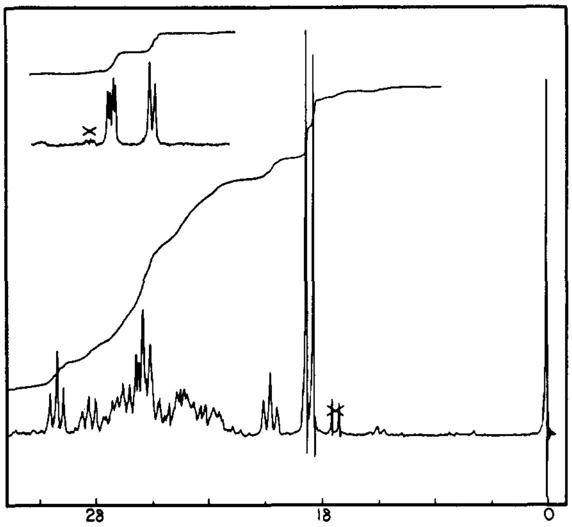

Figure 2. 220-MHz spectrum of IIb in carbon tetrachloride. Peaks marked with X are due to impurities.

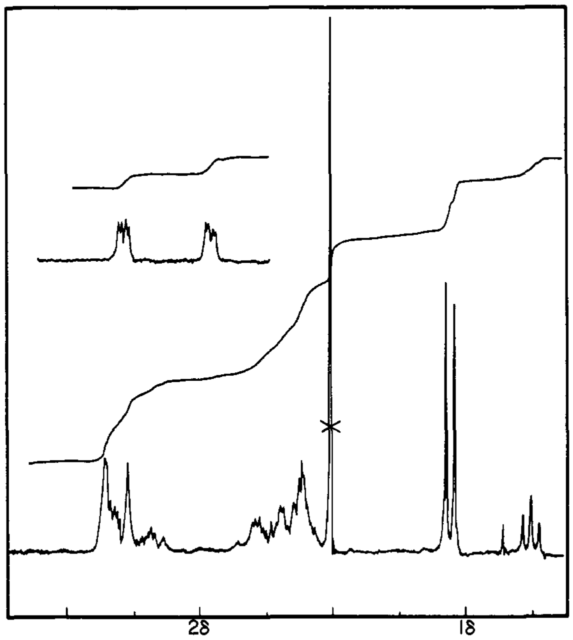

Figure 3. 220-MHz spectrum of III in carbon tetrachloride. Peak marked with X is due to an impurity.

below that previously observed for 1-phenyl-2-butene.

Since the separation of II into its components was only accomplished in the later stages of this research, initial structural data were obtained on the mixture. Mass spectral and elemental analyses showed the mixture to be isomeric with *cis*-I ($C_{12}H_{16}$), with the parent ion at *m/e* 160. The appearance of two methyl doublets of equal height in the nmr spectrum (benzene solvent) gave evidence for there being two components present in about equal amounts. The absence of aryl protons implied gross structural rearrangement; two vinyl hydrogens per molecule were apparent. Hydrogenation of II in ethanol or benzene led to the rapid uptake of 2 equiv while titration with monoperphthalic acid gave a titer of one double bond equivalent. This suggests that the second site of unsaturation is a cyclopropyl ring, and indeed, hydrogenation in a *tert*-butylamine–hexane system gave selective reduction to a dihydro product showing neither vinyl hydrogens nor signals ($<\delta$ 2.3) that might be caused by allylic protons (there is again an equal pair of methyl doublets). The ir spectrum of the dihydro product also shows no evidence for an olefinic function. The uv spectrum of the original photoproduct II has a λ_{max} at 213 nm (ϵ 3500), characteristic of a vinyl cyclopropane chromophore.[7,8]

The preparative separation of II into its two components (IIa and IIb) was eventually accomplished on a glc column of 4,4′-azoxydianisole, used at a temperature at which it is in the nematic phase (*i.e.*, liquid crystal). The two pure photoproducts each analyzed for $C_{12}H_{16}$ and gave molecular ions at *m/e* 160. Compound IIa has a shoulder in its uv spectrum at 213 nm (ϵ 3610, cyclopentane); compound IIb has a shoulder at 207 nm (ϵ 5090). Assignments of structures were conclusively made on the basis of 220-MHz nmr spectra and decoupling at 100 MHz as described below, and confirmed by the isolation and identification of a single (different) pyrolysis product from each of the two isomers (see below).

C. Photolysis of *trans*-I. Photolysis of a 1×10^{-2} *M* solution of *trans*-I in cyclopentane gave rise to one major photoproduct, III, in addition to trans → cis isomerization. The new product analyzed as an isomer of the starting material and its structure was assigned on the basis of nmr data described below.

D. Structures and Nmr Spectra of Photoproducts IIa, IIb, and III. The structural formulas assigned to these photoproducts are the 1,3 cycloadducts shown below.[9] Their 220-MHz[10] spectra are shown in Figures 1, 2, and 3 and the chemical shifts compiled in

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(7) K. S. Wilzbach and L. Kaplan, *J. Amer. Chem. Soc.*, **88**, 2066 (1966).

(8) O. L. Chapman, G. W. Borden, R. W. King, and B. Winkler, *ibid.*, **86**, 2660 (1964).

(9) The correct nomenclature for these compounds is as follows: IIa, 7-*exo*-methyl-6-*endo*-*H*-tetracyclo[6.2.1.0.^{2,11}0.^{2,6}]-9-undecene; IIb, 3-*exo*-methyl-4-*endo*-*H*-tetracyclo[6.2.1.0.^{2,11}0.^{4,8}]-9-undecene; III, 3-*endo*-methyltetracyclo[3.2.1.0^{2,8}3.^{4,8}]-6-undecene. The numbering used in the nmr discussion has been simplified and arranged so as to facilitate the presentation of the data.

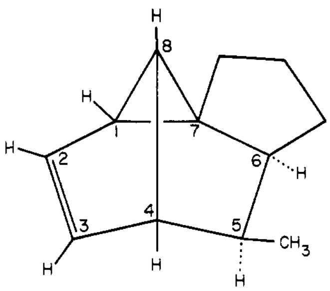
(10) We are grateful to Mr. A. Clouse and Professor J. Crandell of Indiana University for arranging our use of the 220-MHz spectrometer.

Table I. Chemical Shifts of Photoproducts from 6-Phenyl-2-hexene and Model Systems[a]

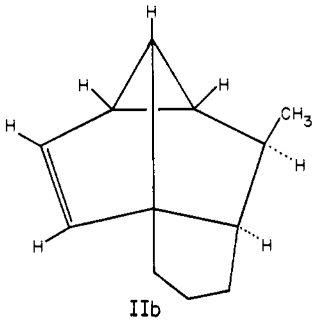
	IIa	IIb	III	IV[b]	V[c]	VI[d]	VII[d]
δ_1	1.86	1.76	2.35	1.92	1.62	1.62	1.70
δ_2	5.51	5.51	5.77	5.47	5.58	5.55	5.57
δ_3	5.27	5.28	5.43	5.29	5.48	5.30	5.41
δ_4	2.78		2.27	3.04	2.83	2.69	2.86
δ_5	1.96_n	(1.8–1.9)	2.35	~1.7	2.55_x	1.68_n	1.90_x
δ_6	2.21	2.06_n	2.31	~1.7	2.55_x	2.04_x	1.30_n
δ_7		1.22	0.76	1.68	1.75	1.67	1.92
δ_8	2.21	2.17		2.42	2.55	2.66	2.40
δ_{CH_3}	0.93_5	1.05_6	1.06_6		0.99_{5n} 0.78_{6n}	0.99_{5x} 1.11_{6n}	0.73_{5n} 1.09_{6x}

[a] Chemical shifts were obtained at 220 MHz in CCl_4 and are given in parts per million downfield from TMS; n = endo, x = exo. [b] These data are from ref 8. [c] These data are from ref 7. [d] These data are from Table I of ref 11 assuming the alternative assignment suggested in footnote *b* (S. Brownstein, personal communication).

Table I. Included in Table I for purposes of comparison are chemical-shift data for structures IV–VII as extracted from the literature. No attempt was made to analyze the absorptions due to the protons on the trimethylene bridge of our photoproducts, as the chemical-shift differences were small and the spectra were complex even at 220 MHz. Coupling constants for the cycloadducts and two of the model systems are compiled in Table II.



IIa



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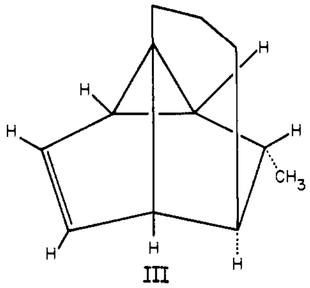
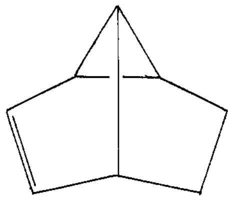
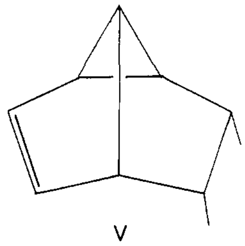


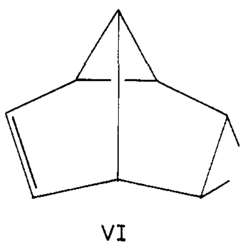
III



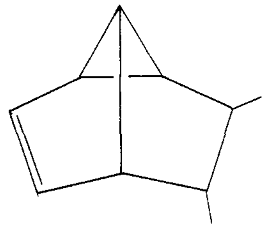
IV



V



VI



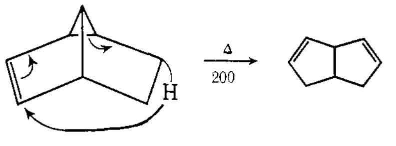
VII

The structures assigned to IIa, IIb, and III are analogous to the intramolecular 1,3 cycloadducts formed upon irradiation of benzene in the presence of olefins[7,11–13] and the gross structural features follow directly from the nmr data.[14] The stereochemistry at C_5 and C_6 has been assigned as follows. For IIa, the low value of J_{45} (0.4 Hz) is consistent with the almost exactly 90° H_4–H_5 dihedral angle one measures from models in which H_5 is endo. The stereochemistry at C_6 follows from several facts: (a) an endo H_6 is consistent with the nature of the IIa pyrolysis (see below), (b) an examination of models suggests that H_6 exo would create considerably more strain in the system (see IIb), and (c) H_6 endo would be the stereochemistry expected for product formation with retention of configuration about the former π bond, as observed for the intermolecular process.[7,11,15]

In IIb, it is J_{67} which is now quite small (~0.8 Hz; appreciable broadening can be detected in the H_6 and H_7 absorptions) and an examination of models indicates that the H_6–H_7 dihedral angle is approximately 100° if H_6 is endo. The 1,5 shift observed upon pyrolysis (see below) confirms this assignment. Retention of configuration about the former π bond would lead to an exo trimethylene bridge (see below) and calculations[16] indicate that an endo linkage would involve an increased strain energy of about 7 kcal/mol.

For III, the 7-Hz coupling between H_6 and H_7 now is indicative of H_6 exo (contrast with IIa above) and geometric restrictions require that the trimethylene bridge be attached exo at C_5.

E. Pyrolysis of IIa and IIb. The structures assigned to IIa and IIb derive support from the observation that they undergo stereoselective thermal rearrangement to dienes, in a manner analogous to that reported[17] for the parent compound VIII (eq 1). Thus, pyrolysis of IIa leads specifically to a new isomer, IXa,



VIII

(1)

while pyrolysis of IIb gives solely the isomeric IXb. The assigned structures were derived from a detailed analysis of the nmr data.[18]

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(11) A. Morikawa, S. Brownstein, and R. J. Cvetanovic, *J. Amer. Chem. Soc.*, **92**, 1471 (1970).

(12) K. S. Wilzbach, A. L. Harkness, and L. Kaplan, *ibid.*, **90**, 1116 (1968).

(13) (a) D. Bryce-Smith, A. Gilbert, and B. H. Orger, *Chem. Commun.*, 512 (1966); (b) *ibid.*, 800 (1969).

(14) Full details of the nmr spectra, decoupling experiments, and derivation of these structures may be found in the doctoral dissertation of William Ferree, Jr., Purdue University, 1971.

(15) The J_{56} value (6.6 Hz) is suggestive of a dihedral angle for these hydrogens approaching 0 or 180°; the former is in fact the case with H_6 endo but coupling to this extent might also be possible for the *ca.* 140° angle associated with H_6 exo.

(16) E. J. Corey and R. S. Glass, *J. Amer. Chem. Soc.*, **89**, 2600 (1967).

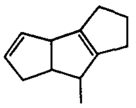
(17) W. R. Roth and B. Peltzer, *Justus Liebigs Ann. Chem.*, **685**, 56 (1965); see also, D. L. Garin, *J. Amer. Chem. Soc.*, **92**, 5254 (1970).

(18) (a) Because of space limitations, the reader is referred to the Ph.D. thesis[2] of W. F. for this analysis. (b) A referee has drawn attention to the possibility of a vinyl cyclopropane–cyclopentane rearrangement preceding the 1,5-hydrogen shift and thus interconverting IIa and IIb. We feel the complete stereoselectivity of these reactions makes such a possibility remote.

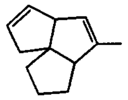
Table II. Coupling Constants and Decoupling Details of Photoproducts from 6-Phenyl-2-hexene and Model Systems[a]

	IIa	IIb	III	IV[b]	V[c]
J_{12}	2.15 {H_1}{H_2}	2.2 {H_2}	2.2 {H_2}	~2	~2
J_{13}	~0.8 {H_1}	~0.8	~0.8 {H_3}	~0.8	
J_{17}		6.7 {H_7}	7 {H_7}		7
J_{18}	6.4 {H_1}	6.8 {H_8}			
J_{23}	5.4	5.25	5.7	6 ± 0.5	5.25–5.5
J_{34}	2.5 {H_4}{H_3}		~2 {H_3}	~2	~2
J_{38}				~0.8	
J_{45}	~0.0 {H_4}		~1		5
J_{48}	5.35 {H_4}				5
J_{56}	6.6	6.3	~0		
J_{67}		~0.8 {H_7}	7 {H_7}		6
J_{78}		6.75 {H_8}			
J_{CH_3}	6.9 {CH_3}	7.0 {CH_3}	7.5 {CH_3}		~7

[a] Coupling constants are given in hertz. Those values derived from decoupling data are accompanied by brackets containing the decoupled protons. [b] Reference 8. [c] Reference 7.



IXa



IXb

F. Quantum Efficiencies for Cycloaddition, Cis → Trans Isomerization, and Disappearance of Starting Material. Because the *trans*-6-phenyl-2-hexene proved difficult to prepare in high purity, all of the quantitative and mechanistic studies were done with *cis*-I. Quantum efficiencies observed were: ϕ_{dis}, 0.29 ± 0.005; ϕ_{II}, 0.26 ± 0.01 (analysis of the nmr spectrum of II indicates that IIa and IIb are formed in approximately equal amounts); and $\phi_{\text{c}\rightarrow\text{t}}$, 0.011 ± 0.004, where ϕ_{dis}, ϕ_{II}, and $\phi_{\text{c}\rightarrow\text{t}}$ represent efficiencies of disappearance, cycloaddition, and cis → trans isomerization, and the uncertainties represent standard deviations of the experimental data. The small difference between ϕ_{dis} and the sum of ϕ_{II} and $\phi_{\text{c}\rightarrow\text{t}}$ seems to be due to the formation of three minor products, all of which appear to have a $\phi \leq 0.01$.

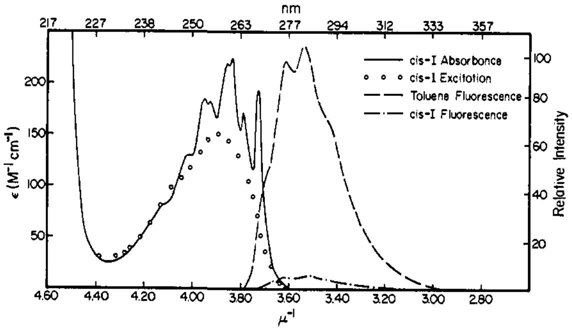


Figure 4. Absorption, excitation, and fluorescence spectra of *cis*-I, with toluene fluorescence included for purposes of comparison. Excitation and fluorescence spectra are corrected; all spectra are at room temperature in cyclopentane.

G. Wavelength Dependence of Cycloaddition. The quantum yields of cycloaddition of *cis*-I were measured upon excitation into the long- and short-wavelength halves of the first electronic absorption band (238–270 nm for ε greater than 50). Irradiation at 262 ± 8 nm (the monochromator produces a triangular distribution of wavelengths) gave a quantum yield of 0.15 while irradiation at 246 ± 8 nm gave a quantum yield of 0.37. These data can be compared to the quantum yield measured at the middle (254-nm mercury resonance line) of these two ranges of 0.26. There is thus a consistent increase in cycloaddition as the aromatic ring is excited into higher vibrational levels within the lowest excited singlet.

H. Sensitized Photolyses of *cis*-I. Benzene-sensitized photolysis of *cis*-I produces both cycloaddition and cis → trans isomerization at approximately equal rates. Sensitization with benzophenone (λ > 330 nm) produces no detectable cycloaddition while isomerization is rapid. Sensitization by acetone (λ = 313 nm) likewise gives cis → trans isomerization unaccompanied by observable cycloaddition.

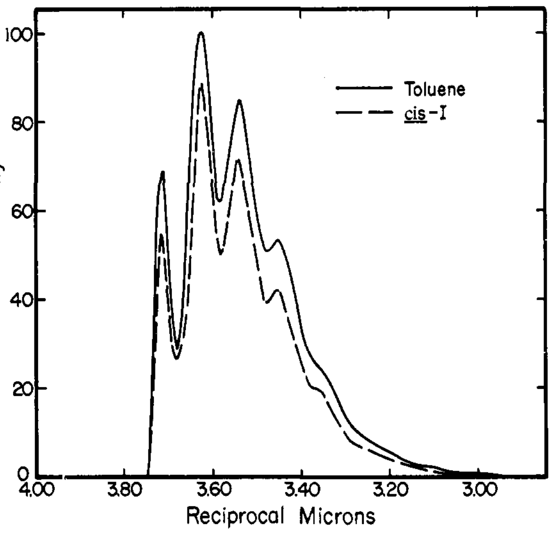


Figure 5. Corrected fluorescence of *cis*-I relative to toluene, at 77°K in an ethanol glass.

I. Spectroscopic Properties of *cis*-I and Homologs. The ultraviolet absorption, fluorescence, and fluorescence excitation spectra of *cis*-I at room temperature in cyclopentane are shown in Figure 4; toluene fluorescence emission is included for purposes of comparison. The absorption spectrum is essentially identical with that of toluene ($\lambda_{\max}$ 261 nm (ε 243)) with $\lambda_{\max}$ 261 nm (ε 225). The extinction coefficient is perhaps better compared with that observed for hexylbenzene, *i.e.*, $\lambda_{\max}$ 262 nm (ε 215). The marked diminution in fluorescence of *cis*-I evident in Figure 4 ($\phi_f = 0.005$ if one assumes $\phi_f = 0.10$ for toluene[19]) is *not* observed

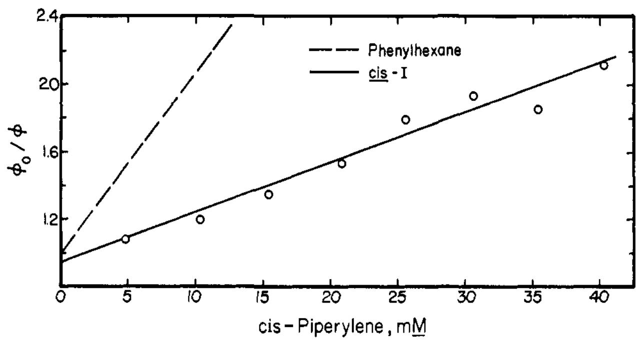


Figure 6. Quenching of fluorescence of 1.14 m*M* *cis*-I by *cis*-piperylene; the plot for phenylhexane is included for purposes of comparison.

when the sample is examined at 77°K in an ethanol glass, *cf.* Figure 5. Comparable "internal quenching" at room temperature is observed for *trans*-I and 5-phenyl-1-pentene but not for 5-phenyl-2-pentene, 6-phenyl-2-hexyne, or hexylbenzene; the data are shown in Table III. No phosphorescence could be observed at 77°K for *cis*-I or 5-phenyl-2-pentene. 6-Phenyl-2-hexyne showed emission with an integrated intensity 97% that of toluene.

Table III. Fluorescence Emission Relative to Toluene

Compound	Fluorescence at room temp^a	Fluorescence at 77°K^b
cis-I	0.05	0.81
trans-I	0.04^c	
5-Phenyl-1-pentene	0.05	
Hexylbenzene	0.90	
5-Phenyl-2-pentene	0.88	0.90
6-Phenyl-2-hexyne	0.72	0.82

^{a} Areas of corrected spectra relative to toluene with concentrations (0.4–0.5 m*M*) adjusted so as to give equal absorbances for all solutions. ^{b} Ethanol glass. ^{c} Determined on an Aminco-Bowman instrument using comparative peak heights at 284 nm.

Attempts to determine the fluorescent lifetime of *cis*-I on a TRW decay-time fluorimeter[20] were unsuccessful, presumably because the lifetime was below the measurable limit (*ca.* 15 nsec). Data obtained for toluene, 5-phenyl-2-pentene, and 6-phenyl-2-hexyne (all *ca.* 2.5 m*M* in cyclopentane) were 30, 24, and 15 nsec, respectively.

Relative lifetime data were obtained by the method of Berlman[21] using oxygen quenching of fluorescence. The results are presented in Table IV. The "relative lifetime" data in Table IV involve no assumptions other than quenching of all compounds at an identical (diffusion-controlled) rate, and compare favorably with the "relative fluorescence intensities" in Table III. The absolute value calculated for toluene (37 nsec) may be compared with our TRW measurement of 30 nsec (see above) and a literature[21] value of 34 nsec; the similarity in these values and the above cited correspondence of relative lifetime and fluorescence intensity data give the other calculated Υ's in Table IV some credence and confirm the short lifetime of *cis*-I.

Table IV. Lifetimes Using Oxygen Quenching of Fluorescence

Compound	ϕ_0/ϕ^a	Υ (rel)^b	Υ (calcd, nsec)^c
Toluene	12.2	(1.00)	37
cis-I	1.75^d	0.067	2.5
6-Phenyl-2-hexyne	8.49	0.67	25
5-Phenyl-2-pentene	10.1	0.81	30
Hexylbenzene	10.7	0.87	32

^{a} Substrate concentrations 0.4–0.5 m*M*, solutions saturated with oxygen. ^{b} Relative values of $[(\phi_0/\phi) - 1]$. ^{c} Calculated using the Stern–Volmer expression $\Upsilon = [(\phi/\phi) - 1]/[O_2]kq$, with $[O_2]$ estimated as $2.0 \times 10^{-2} M$[22] (cyclopentane) and *kq* assumed[21] to be diffusion controlled, *i.e.*, $1.5 \times 10^{10}\ M\ \text{sec}^{-1}$. ^{d} Average of four measurements; a fifth measurement at 6.6 m*M* gave a comparable value.

We have elsewhere[1] reported the efficient fluorescence quenching of benzenoid hydrocarbons by *cis*-piperylene and such a study with *cis*-I gave Stern–Volmer data (corrected for piperylene absorption) plotted in Figure 6 (the plot for hexylbenzene[23] is superimposed for purposes of comparison). The slope is 29.7 ± 2.3 M^{-1} but the large corrections required and the weakness of emission give this slope a greater uncertainty than the standard deviation would indicate. Because *chemical* quenching by piperylene was examined at about 6 m*M* substrate concentrations, fluorescence quenching was likewise examined at 6.7 m*M* *cis*-I. This necessitated the use of higher concentrations of piperylene, which in turn gave rise to a Stern–Volmer plot showing upward curvature, presumably due to an inner filter effect.[24] Corrections for this effect are quite large beyond 20 m*M* piperylene and the slope (11.2 M^{-1}) was estimated from the first two points (8.4, 19.1 m*M*) only. Since comparison with the chemical data is of prime import and since the low *cis*-I concentration data contain large uncertainties, a fluorescence quenching slope of 11 M^{-1} will be assumed for purposes of discussion.

In addition to fluorescence quenching by oxygen and *cis*-piperylene, quenching by acetone (8.06, 11.8, and 16.4 m*M* quencher) at 6.6 m*M* *cis*-I was also measured. The estimated Stern–Volmer slope is 60 M^{-1} (using an assumed intercept of 1.00 because of the few data points available).

J. Effect of Oxygen on *cis*-I Photochemistry. The effect of oxygen on both cycloaddition and cis → trans isomerization was examined. It was found that whereas fluorescence is quenched by 42.5 ± 1.6% in an oxygen saturated solution, cycloaddition is quenched by 28.9 ± 2.1% and remarkably, cis → trans isomerization increases by a factor of 4.1 ± 0.3 (*i.e.*, $\phi_{c\rightarrow t}(O_2) = 0.044$). The material balance in these experiments is unchanged from that observed with degassed samples. The possibility of sensitized cis → trans isomerization by an intermediate formed *via* oxidation was ruled out by an experiment in which oxygen-saturated samples were irradiated for one-half the normal time, saturated with argon, and irradiated for a second half-interval. It was observed that the oxygen-increased rate of isomerization did *not* continue into the second half-interval; *in fact, the data quantitatively show that the average*

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

(20) We are grateful to Professor Fred Lytle for the use of his lifetime fluorimeter.

(21) I. B. Berlman, "Handbook of Fluorescence Spectra of Aromatic Molecules," Academic Press, New York, N. Y., 1965.

(22) Y. Kobatake and J. Hildebrand, *J. Phys. Chem.*, **65**, 331 (1969); J. E. Jolley and J. Hildebrand, *J. Amer. Chem. Soc.*, **80**, 1050 (1958).

(23) P. Froehlich, unpublished data.

(24) C. A. Parker, "Photoluminescence of Solutions," Elsevier, New York, N. Y., 1968.

amount of isomerization observed is exactly the amount expected on the basis of the known rates of isomerization in oxygen and argon-saturated samples and the light absorbed in each half-interval.

K. Effect of Piperylene on *cis*-I Photochemistry. *cis*-Piperylene was found to quench both cycloaddition and cis → trans isomerization but inefficiently; Stern–Volmer slopes for the two processes were 4.5 ± 1.3 M^{-1} (Figure 7) and 11 ± 6 M^{-1}, respectively (the deviation in the latter figure reflects difficulty in observing small changes in the highly inefficient isomerization process). Interestingly, no significant quenching of cis → trans isomerization in oxygen-saturated solutions could be observed.

Chemical quenching thus seems to be, if anything, *less* efficient than fluorescence quenching, whereas a triplet energy transfer component would have been expected to lead to a *higher* chemical quenching efficiency. The absence of significant triplet energy transfer was confirmed by a "triplet counting" experiment whereby the phenylhexene-sensitized isomerization of piperylene was measured.[25,26] The data are presented in Table V together with data for toluene-, hexylbenzene-, and oxygen-saturated solutions of *cis*-I; ϕ_{et} represents the quantum efficiency for triplet energy transfer to piperylene and is given first with correction for isomerization caused by light absorption by the diene (raw) and second as corrected for singlet quenching by piperylene (corr).

Table V. Triplet Counting with *cis*-Piperylene[a]

Compd	ϕ_{et}(raw)[b]	ϕ_{et}(corr)[c]
cis-I	0.0049	0.0057
	0.0039	0.0046
	Av	0.0052
cis-I	0.023	0.027
(O_2 satd)	0.020	0.023
	Av	0.025
Toluene	0.076	0.34
Hexylbenzene	0.134	0.38

[a] Substrate concentrations were *ca.* 20 m*M*, piperylene concentrations *ca.* 18 m*M*. All solutions were degassed with argon except where noted. [b] Corrected for isomerization due to light absorbed by piperylene and for back reaction of the diene. [c] Corrected further for singlet (fluorescence) quenching of the substrate by piperylene using Stern-Volmer slopes of 11, 200, and 106 M^{-1} for phenylhexene, toluene,[23] and hexylbenzene.[23]

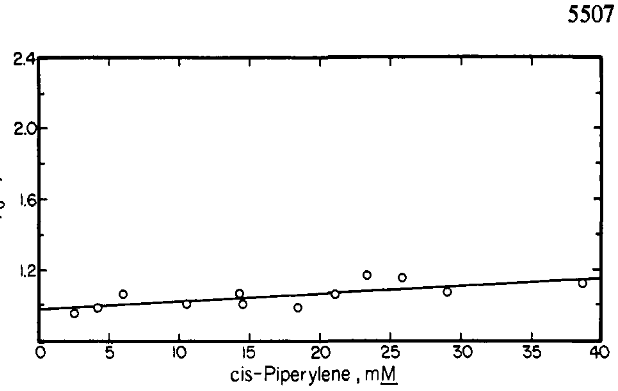

Figure 7. Quenching of *cis*-I cycloaddition by *cis*-piperylene.

If one assumes complete capture of substrate triplets by the piperylene, the ϕ_{et} (corr) values should approximate ϕ_{Ic} for the substrates. Although a complete study of ϕ_{et} as a function of piperylene concentration was not attempted, the value for toluene compares favorably with the estimated ϕ_{Ic} value of 0.30 using 2-heptene[1] and the value of 0.36 estimated for the phenyl moiety in 1-phenyl-2-butene.[1] Note that ϕ_{et} is increased in the presence of oxygen, but the lack of a concomitant increase in piperylene quenching of cis → trans isomerization in the presence of oxygen leaves the source of this higher ϕ_{et} value in doubt. Of prime import, of course, is the observation that *few cis-I triplets are trapped by piperylene* and *triplet energy transfer is too small to account for the chemical quenching by this diene.*

Finally, a quenching experiment using acetone as quencher was carried out, for purposes of comparison with the fluorescence quenching by this ketone cited above. A Stern–Volmer slope of 29 M^{-1} was obtained upon plotting the data.

Discussion

The primary observations reported in the Results may be summarized as follows. It has been established that the photochemistry of 6-phenyl-2-hexene consists primarily of internal cycloaddition together with some cis → trans olefin isomerization. The cycloadducts (IIa, IIb, III) arise from 1,3 addition to the aromatic ring, as has been observed for intermolecular systems, and are formed with retention of configuration about the former π bond. The cycloaddition is efficient ($\phi_{254\ nm}$ = 0.26) but the double bond isomerization markedly less so ($\phi_{c\rightarrow t}$ = 0.011; compare $\phi_{c\rightarrow t}$ = 0.16 for 1-phenyl-2-butene[1,4e]). Quenching of cycloaddition is minimal and appears to be less efficient than the quenching of phenylhexene fluorescence—the lack of correspondence between these two phenomena has previously been noted by ourselves[1] and others[5e] for the 1-phenyl-2-butene system. Furthermore, very few triplets are detectable by energy transfer to *cis*-piperylene, an observation *not* attributable to rapid internal triplet energy transfer, since by contrast with 1-phenyl-2-butene, 6-phenyl-2-hexene cis–trans isomerization is too inefficient to account for the *ca.* 30% intersystem crossing one would ordinarily expect for the toluene chromophore[28] (however, see below). A wavelength effect

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

[26] Use of this method at 254 nm requires corrections that have not been considered in prior work,[19,25] in that *cis*-piperylene absorbs light and directly photoisomerizes at a significant rate, requiring that the quantum yield for this process be determined for calculation of the appropriate correction.

The procedure chosen to obtain the quantum yield was to first determine the effective path length, *l*, in the Vycor photolysis tubes by irradiating dilute and concentrated solutions of *cis*-I to measure formation of II with the known quantum yield (0.26). This provided a direct measure of the absorbance of the tubes at high and low absorbance, and *l* was calculated to be 1.35 cm by Beer's law. With *l* having been determined the quantum yield for direct isomerization of *cis*-piperylene in dilute (0.018 *M*) solution was measured as 0.090 (average of 0.094 and 0.086), which was later confirmed by others.[27] A simpler procedure would have been to irradiate *cis*-piperylene at concentrations high enough to absorb all the light, but the chosen procedure had the advantage of using the same concentration used in the triplet counting experiments, minimizing possible error from bimolecular reactions at higher concentrations, and provided an experimentally useful number (*l*).

[27] J. Saltiel, L. Metts, and M. Wrighton (*J. Amer. Chem. Soc.*, 92, 3227 (1970)) report $\phi_{c\rightarrow t}$ = 0.091, $\phi_{t\rightarrow c}$ = 0.115; S. Boue and R. Srinivasan (*ibid.*, 92, 3226 (1970)) report $\phi_{c\rightarrow t}$ = 0.100, $\phi_{t\rightarrow c}$ = 0.083.

[28] Considering the triplet energies of the two chromophores (*ca.* 83 and 80 kcal/mol for toluene and olefin), an interaction between phenyl

on cycloaddition is observed and it is such that *higher frequency irradiation increases cycloaddition efficiency*, the variation in incident wavelength being constrained to portions of the lowest energy ("B" band) electronic transition. Finally, sensitization of cis → trans isomerization in the absence of cycloaddition may be effected, thus ruling out addition of triplet olefin to the aromatic ring.

Some clue as to the source of these phenomena may be derived from the spectroscopic properties of 6-phenyl-2-hexene. The uv absorption spectrum is unexceptional and lends credence to our supposition of minimal ground-state interaction between the chromophores. However, the fluorescence spectrum, though similar to that of hexylbenzene in appearance, shows a remarkable (94%) diminution in intensity by comparison with the saturated analog; such a reduction is not observed with either 1-phenyl-2-butene or 5-phenyl-2-pentene (by contrast, all three aryl olefins show no phosphorescence emission). Since the intensity of $S_0 \rightarrow S_1$ absorption for the phenylhexene is not markedly different from hexylbenzene, there is no reason to believe that radiational decay (k_f) is unusually rapid for this system, and it would therefore seem that competitive decay mode(s) have somehow shortened the singlet lifetime. This is, in fact, observed in that there is a 92% reduction in singlet state lifetime for the phenylhexene by comparison with hexylbenzene.

An analogy for this surprising result may be found in the report by Hirayama[29] on diphenylalkanes of the general formula $Ar(CH_2)_nAr$, wherein he observed that compounds for which $n = 3$ show (a) much reduced (95–98%) phenyl monomer fluorescence and (b) characteristic long-wavelength emission attributable to an intramolecular excimer.[30] This phenomenon occurs in the absence of perturbation of the uv absorption spectra and is specific for $n = 3$ (compounds with $n = 1$–6 were examined). The similarity to our system extends to monomer singlet lifetime (we calculate $\Upsilon = 3$ nsec for diphenylpropane from oxygen quenching data in the literature[29]) and the absence of interaction in rigid media at low temperature (*i.e.*, 1,3-diphenylpropane shows minimal excimer and fully restored monomer fluorescence; the intensity of 6-phenyl-2-hexene fluorescence likewise is restored to a normal value).[31] Hirayama presents a conformational analysis of the diphenylalkanes which predicts an optimum opportunity for coplanarity (and complexation) of the two π systems with minimal steric interaction of alkane chain hydrogens when $n = 3$. An identical argument can be made for the 6-phenyl-2-hexene with exciplex[32] formation[33] resulting from interaction between the phenyl excited singlet state and ground-state olefin.[34,35] Rapid formation of the exciplex followed by radiationless decay to ground-state phenylhexene would thus represent a reasonable explanation[33] for the limited fluorescence[36] and short singlet lifetime of the aryl olefin.

The obvious question then is whether formation of the exciplex competes with or precedes formation of one or more of the photoproducts. There is an increasing amount of evidence that singlet excimer[37] and exciplex[38] formation may commonly precede solution phase photodimerization and photocycloaddition, respectively. There is also reason to postulate that the internal cycloaddition of 6-phenyl-2-hexene is singlet derived. Thus, the cycloaddition can be quenched by oxygen, piperylene, and acetone whereas olefin cis–trans isomerization is actually enhanced by oxygen. Furthermore, this chemical quenching is about one-half as efficient as fluorescence quenching, thus suggesting at least partial involvement of a short-lived (unquenchable) precursor to cycloaddition. This conclusion derives support from the wavelength studies which clearly show that cycloaddition[39] efficiency *increases*[40] with higher frequencies of incident light, irradiation being constrained to the lowest electronic transition. Although it is claimed[41] that benzenoid aromatics in solution show no dependence of intersystem crossing on the vibrational level of S_1 initially populated,[42] gas-phase data for toluene[43] clearly suggest that intersystem crossing *decreases* upon excitation into higher vibrational levels.

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triplet and ground-state olefin *not* involving triplet energy transfer is considered unlikely.

(29) F. Hirayama, *J. Chem. Phys.*, **42**, 3163 (1963).

(30) Similar observations have now been reported for other $R(CH_2)_3R$ systems: (a) D. T. Browne, J. Eisinger, and N. J. Leonard, *J. Amer. Chem. Soc.*, **90**, 7302 (1968); (b) N. J. Leonard, H. Iwamura, and J. Eisinger, *Proc. Nat. Acad. Sci. U. S.*, **64**, 352 (1969); (c) E. A. Chandross and C. J. Dempster, *J. Amer. Chem. Soc.*, **92**, 3586 (1970); (d) Von W. Klopfer, *Ber. Bunsenges. Phys. Chem.*, **74**, 693 (1970).

(31) This temperature effect has also been observed for 1,3-dinaphthylpropane and attributed to an activation energy for self-quenching.[30c]

(32) J. B. Birks, *Nature* (*London*), **214**, 1187 (1967).

(33) L. M. Stephenson, D. G. Whitten, G. F. Vesley, and G. S. Hammond, *J. Amer. Chem. Soc.*, **88**, 3665 (1966); L. M. Stephenson and G. S. Hammond, *Pure Appl. Chem.*, **16**, 125 (1968); L. M. Stephenson and G. S. Hammond, *Angew. Chem., Int. Ed. Engl.*, **8**, 261 (1969).

(34) Such exciplex formation is presumably responsible for the singlet quenching observed when benzene (K. E. Wilzbach and L. Kaplan, private communication; A. Morikawa and R. J. Cvetanovic, *J. Chem. Phys.*, **49**, 1214 (1968)) and toluene (*cf.* ref 1) are irradiated in the presence of simple olefins.

(35) There is now ample evidence that internal fluorescence quenching of aromatics by olefins is commonplace in bicyclic systems, a fact which is undoubtedly intimately related to the photochemistry of these compounds. See G. R. Ziegler, *J. Amer. Chem. Soc.*, **91**, 446 (1969); R. C. Hahn and L. J. Rothman, *ibid.*, **91**, 2409 (1969); J. R. Edman, *ibid.*, **91**, 7103 (1969). See also, H. E. Zimmerman and C. O. Bender, *ibid.*, **92**, 4366 (1970).

(36) See ref 5d for a similar observation with 7-phenyl-2,4-heptadienes.

(37) (a) A. Dammers-de-Klerk, *Mol. Phys.*, **1**, 141 (1958); (b) H. Morrison, H. Curtis, and T. McDowell, *J. Amer. Chem. Soc.*, **88**, 5415 (1966); (c) R. Hoffman, P. Wells, and H. Morrison, *J. Org. Chem.*, **36**, 102 (1971); (d) J. Eisinger and A. A. Lamola, *Biochem. Biophys. Res. Commun.*, **28**, 558 (1967); (e) D. O. Cowan and R. L. Drisko, *J. Amer. Chem. Soc.*, **89**, 3068 (1967); (f) J. S. Bradshaw, N. B. Nielsen, and D. P. Rees, *J. Org. Chem.*, **33**, 259 (1968); (g) P. Wilairat and B. Selinger, *Aust. J. Chem.*, **21**, 733 (1968); (h) B. K. Selinger and M. Sterns, *Chem. Commun.*, 978 (1969); (i) H. Nozaki, I. Otani, R. Noyori, and M. Kawanisi, *Tetrahedron*, **24**, 2183 (1968); (j) C. D. De Boer and R. H. Schlessinger, *J. Amer. Chem. Soc.*, **90**, 803 (1968); (k) R. Lisewski and K. L. Wierzchowski, *Chem. Commun.*, 348 (1969); (l) J. Christie and B. Selinger, *Photochem. Photobiol.*, **9**, 471 (1969); (m) E. A. Chandross and C. J. Dempster, *J. Amer. Chem. Soc.*, **92**, 703 (1970), and ref 30c.

(38) See, for example: (a) L. A. Singer and G. A. Davis, *J. Amer. Chem. Soc.*, **89**, 598 (1967); (b) R. J. McDonald and B. K. Selinger, *Tetrahedron Lett.*, 4791 (1968); (c) ref 4g; (d) H. Bouas-Laurent and R. Lapanyade, *Chem. Commun.*, 817 (1969); (e) W. H. F. Sasse, *Aust. J. Chem.*, **22**, 1257 (1969); (f) R. M. Bowman, T. R. Chamberlain, C. W. Huang, and J. J. McCullough, *J. Amer. Chem. Soc.*, **92**, 4106 (1970); (g) J. C. Dalton, P. A. Wriede, and N. J. Turro, *ibid.*, **92**, 1318 (1970); (h) O. L. Chapman and R. D. Lura, *ibid.*, **92**, 6352 (1970).

(39) A combination of inefficiency for cis–trans isomerization and low-light intensity from the monochromator prevented a similar study for this reaction.

(40) This is opposite to the wavelength dependence reported for butene cycloaddition to benzene in the gas phase; *cf.* L. Kaplan and K. E. Wilzbach, *J. Amer. Chem. Soc.*, **90**, 3291 (1968). See also, D. Anderson, *J. Phys. Chem.*, **74**, 1686 (1970).

(41) C. L. Braun, S. Kato, and S. Lipsky, *J. Chem. Phys.*, **39**, 1645 (1963); J. B. Birks in "Molecular Luminescence," E. C. Lim, Ed., W. A. Benjamin, New York, N. Y., 1969, p 219; see also, M. D. Lumb, C. L. Braga, and L. C. Pereira, *Trans. Faraday Soc.*, **65**, 1992 (1969).

(42) For a contrary view, see V. M. Berenfel'd and V. A. Krongauz, *Izv. Akad. Nauk SSSR Ser. Fiz.*, **32**, 1575 (1968).

Furthermore, the constancy of the ratio ϕ_f/ϕ_{lc} as wavelength is varied[43] implicates the lowest vibrational level as the source of both phenomena[42] and the same conclusion may be drawn for the solution phase by noting that the ϕ_{lc} values for toluene and hexylbenzene become comparable only after correction is made for singlet (fluorescence) quenching (see Results). Thus, the wavelength dependence for cycloaddition would seem to be more consistent with the involvement of a singlet rather than a triplet species.

There is other evidence to support this view. The retention of configuration at the reacting π bond argues against a triplet diradical intermediate and it has been suggested[44] that 1,3 cycloaddition of benzene to olefins is symmetry allowed for benzene in its S_1 state but forbidden in the T_1 state. Intermolecular cycloaddition in solution requires very high olefin concentrations[7,12,13a] whereas less than 10^{-1} M 2-heptene traps essentially all toluene triplets capable of sensitizing isomerization without producing cycloadducts.[1] The cycloaddition of benzene to 2-butene in the gas phase has likewise been recently attributed to the benzene S_1 state.[11]

If one accepts that both exciplex formation and cycloaddition arise from the S_1 state, it is a reasonable (though not requisite) extension to our suggestion[4f] of the exciplex as a precursor to the cycloadducts. In fact, an "$n = 3$ rule" for facile internal cycloaddition of $R(CH_2)_nR'$ systems is rapidly developing, with $R = R'$ = thymyl[45] and naphthyl[30c,37m] having recently been reported. Internal dimerization of both systems *via* excimer precursors is suggested.[30a,30c,46–48]

As discussed above, at least some portion of the cycloaddition must be arising from upper vibrational levels of S_1; on the other hand, the fact that the chemical reaction can be quenched at all and the significant shortening of the singlet lifetime argue for considerable involvement of the lowest (fluorescing) vibrational level of S_1.[51] Thus, it is generally assumed[52] that radiationless decay of vibrational states proceeds at rates of *ca.* 10^{12} sec^{-1}, far too rapidly for external quenching to compete. However, the diminished oxygen quenching of cycloaddition that is observed (29% by comparison with 43% fluorescence quenching), could reflect a combination of partial quenching of cycloaddition from the vibrationally equilibrated S_1 state and zero quenching of reaction occurring from upper levels. Calculations[53] based on this view yield an estimate of 67% of cycloaddition arising from the lowest vibrational level (*i.e.*, $\phi = 0.17$ at 254 nm) with the remainder ($\phi = 0.09$ at 254 nm) occurring from upper levels. Interestingly, excitation at 262 nm (not far from the estimated[43] 0–0 transition for toluene of 266.8 nm) produces cycloaddition with $\phi = 0.15$, in rather good agreement with the 0.17 estimated above for the lowest vibrational level. Such involvement of upper vibrational levels in solution photochemistry is, at first sight, surprising though by no means unique.[54] What it does point out is the potential rapidity of interaction between chromophores in nonconjugated bichromophoric molecules, a phenomenon somewhat akin to the situation in the vapor phase, where the vibronic level initially populated may play a significant role in the ultimate fate of the excited molecule.[43] Clearly, the differential involvement of vibrational levels in solution photochemistry deserves further study.

Having decided that exciplex formation followed by cycloaddition[55] constitutes the principal reaction path, we are left with the task of explaining the relatively small amount of cis → trans isomerization that is observed ($\phi_{c\rightarrow t} = 0.011$). The motivation for a study of this particular molecule originated with the intent to extend our observations of internal triplet energy transfer in 1-phenyl-2-butene,[1,4b,c,e] and our inclination is to view the cis–trans isomerization of 6-phenyl-2-hexene as a consequence of the same phenomenon, *i.e.*, excitation of the phenyl chromophore, intersystem crossing to the triplet, energy transfer to the olefin, and decay of the (twisted) olefin triplet to cis and trans ground-state isomers.[4e] In this view, the low efficiency for cis–trans isomerization of the phenylhexene would be primarily a consequence of diminished intersystem crossing from the short-lived aryl singlet, the absence of phosphorescence[56] being indicative of rapid and probably complete internal energy transfer for those triplets that do form. Thus, one can calculate that were intersystem crossing to be *ca.* 3.4 times as efficient as fluorescence (the ratio of ϕ_{lc}/ϕ_f observed for toluene, see Results), 6-phenyl-2-hexene should form triplets with a ϕ_{lc} of 3.4 ± 0.005 or 0.017. If one assumes complete triplet transfer and a decay ratio of one for the twisted olefin triplet, a ϕ_{lc} of 0.017 would lead to a $\phi_{c\rightarrow t}$ of 0.0085, a value in reasonable agreement with the efficiency (0.011) actually observed.

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(43) For example, see C. S. Burton and W. A. Noyes, Jr., *J. Chem. Phys.*, **49**, 1704 (1968); F. S. Wettack and W. A. Noyes, Jr., *J. Amer. Chem. Soc.*, **90**, 3901 (1968); J. C. Hemminger and E. K. C. Lee, *J. Chem. Phys.*, **54**, 1405 (1971).

(44) D. Bryce-Smith, *Chem. Commun.*, 806 (1969).

(45) N. J. Leonard, K. Golankiewicz, R. S. McCredie, S. M. Johnson, and I. C. Paul, *J. Amer. Chem. Soc.*, **91**, 5855 (1969).

(46) A particularly intriguing report is the recent observation of cyclobutane formation upon irradiation of 3,7-dimethylenebicyclo-[3.3.1]nonane; *cf.* A. G. Yuchenko, A. T. Voroshchenko, and F. N. Stepanov, *Zh. Org. Khim.*, **6**, 189 (1970). The double bonds are here held rigidly coplanar.

(47) We see no sign of cycloadducts when $n = 1$ or 2 in the aryl olefin series; other examples of $n = 3$ have been observed in our laboratories but product structures have not been completely assigned. Systems involving $n > 3$ are under study. 6-Phenyl-2-hexyne gives a cycloadduct also currently under study.

(48) A 1,3 diradical ("prefulvene") has been suggested[49] as the precursor to olefin cycloaddition to benzene, but attempts to trap such a species have so far been without success (A. Gilbert, private communication). Benzvalene, considered[12,50] to be the principle intermediate leading to positional isomerization of substituents on the benzene ring, has been ruled out[12] as an intermediate for cycloaddition because of the inefficiency of its formation by comparison with cycloaddition.

(49) D. Bryce-Smith, A. Gilbert, and H. C. Longuet-Higgins, *Chem. Commun.*, 240 (1967).

(50) R. B. Cundall and J. R. Voss, *ibid.*, 902 (1968).

(51) We are assuming that the exciplex, once formed, is not quenched but either decays to ground-state phenylhexene or goes on to photoproducts.

(52) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," Wiley, New York, N. Y., 1966, p 277. See also, P. M. Rentzepis, *Photochem. Photobiol.*, **8**, 579 (1968).

(53) Oxygen quenches 43% of fluorescence and 29% of cycloaddition. The nonquenchable fraction of cycloaddition (1 − 0.29) will be equal to the fraction produced in the upper levels (X) plus the product of the fraction of the fluorescent level that is not quenched (1 − 0.43) times the number of singlets reaching the fluorescent level; $X = 0.33$.

(54) See, for example, R. S. Becker, E. Dolan, and D. E. Balke, *J. Chem. Phys.*, **50**, 239 (1969). The system discussed here involves a "unimolecular" decomposition as opposed to the bichromophoric interaction of the phenylhexene.

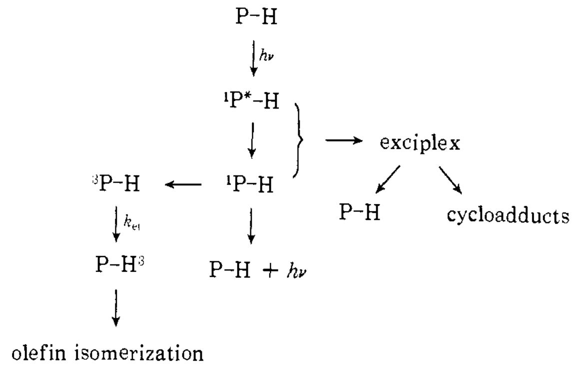
(55) To the extent that this sequence is valid for *intra*molecular reaction, it should be equally applicable to *inter*molecular cycloadditions.

(56) Phosphorescence was sought under conditions (ethanol glass) where we have shown intermolecular triplet quenching by an olefin to be minimal.

Further support for this picture can be derived from several observations. First, isomerization is enhanced by oxygen, a result most easily rationalized by invoking oxygen enhancement of phenyl intersystem crossing.[11] Second, the inability to observe effective quenching by piperylene over and above that involving the singlet state further argues for a rapid internal transfer step. Similarly, the detection of but few triplets with piperylene ($\phi_{\mathrm{et}} \leq 0.005$), confirms that those triplets which do form rapidly interact with the double bond. In fact, one can use the above data to estimate a *minimum* rate constant for the *internal* transfer step: since ϕ_{lc} is estimated to be 0.017 and $\phi_{\mathrm{et}} \leq 0.005$, a *maximum* of 29% of the aryl triplets are captured by 0.018 *M* piperylene. Assuming the *external* transfer to be diffusion controlled at 1.5×10^{10} M^{-1} sec^{-1}, the rate constant (k_{et}) for *internal* transfer must be $\geq 9 \times 10^{8}$ sec^{-1}. This is certainly a minimum value, because the extent of piperylene isomerization when compared with piperylene quenching (after correction for singlet quenching), suggests that some portion of the sensitized diene isomerization may result from singlet interactions, trace impurities, etc. The rate constant calculated above ($\geq 9 \times 10^{8}$ sec^{-1}) may be compared to that calculated in like fashion[1] for 1-phenyl-2-butene ($\geq 3.6 \times 10^{9}$ sec^{-1}) and rate constants of 7.2×10^{10} to 3.3×10^{9} sec^{-1} recently estimated[5b] for internal transfer from a benzoyl to a styrene chromophore over 2–4 methylene units.[57,58]

Finally, some further comment on our observation of diminished intersystem crossing in the 6-phenyl-2-hexene molecule is warranted. There is good reason to believe that the inhibition of intersystem crossing in such bichromophoric systems is not peculiar to the aryl olefin. Thus we have made similar observations for a nonconjugated keto olefin (5-hepten-2-one[4g,4i,59]) and a nonconjugated benzoyl olefin (1-phenyl-4-hexen-1-one[59]). An apparently analogous effect has been recently reported by several groups for nonconjugated benzoyl and phenyl ketones[60] and may be an important factor in the photochemistry of a variety of bicyclic systems.[29] *In sum, it seems clear that a principle consequence of the interaction between nonconjugated chromophores may be to greatly accelerate singlet decay and chemical reaction, thereby modifying the photochemistry of these molecules significantly.*

The photochemical and photophysical processes discussed above are schematically displayed below, where P–H represents 6-phenyl-2-hexene, ^{1}P*–H and ^{1}P-H represent the vibrationally excited and equilibrated phenyl singlet excited states, and ^{3}P–H and P–H^3 represent the triplet state localized either on the phenyl or hexenyl moieties. It is our feeling that intermolecular cycloaddition proceeds through the same sequence of exciplex formation followed by bond formation.



Experimental Section

Instrumentation. Infrared spectra were recorded with a Perkin-Elmer Model 221 spectrometer or a Perkin-Elmer Infracord Model 137 spectrometer and calibrated with the polystyrene film bands at 6.238 and 3.303 μ. Uv spectra were determined with a Cary Model 14 recording spectrometer; photochemical solvent transparencies in the uv were checked on a Bausch and Lomb Model 505 spectrometer. Nmr spectra were obtained on a Varian A-60 spectrometer (except for the detailed studies on the structures of IIa, IIb, III, and the thermolysis products of IIa and IIb obtained on Varian 100-MHz and Varian 220-MHz spectrometers) and chemical shifts are reported in parts per million downfield from tetramethylsilane as internal standard (δ). The abbreviations s, d, t, q, and m refer to singlet, doublet, triplet, quartet, and multiplet; the coupling constant (J) is measured in hertz. Mass spectra were measured with a Hitachi RMU-6A spectrometer at an ionizing voltage of 75 eV unless otherwise noted. Melting points were obtained on a calibrated Fisher-Johns melting point apparatus. Microanalyses were performed by Dr. Yeh of this department.

A Hanovia low-pressure mercury resonance lamp (688A-45) emitting at 253.7 nm was employed for the preparative photolyses and turntable experiments except where otherwise noted. The lamp is made from Vycor glass which removes the 184.9-nm emission line, and is contained in a quartz immersion tube sealed to a 60–50 ground glass joint. In certain experiments, a 450-W Hanovia type L mercury arc lamp or a 200-W Hanovia mercury arc lamp was used. The turntable used for these experiments is described in detail in the thesis of R. W. Peiffer;[61] Vycor test tubes were used.

Some experiments were performed on a Bausch and Lomb High Intensity Monochromator (No. 33-87-25-01) which has entrance and exit slits which are adjustable from 0.0 to 6.0 mm and a uv grating which was 2700 grooves/mm and a dispersion of 3.2 nm/mm of exit slit opening. The source is a 150-W super pressure mercury arc (Bausch and Lomb SP-200, L-1). The reaction vessel for this light source is a water-jacketed cell with flat quartz (Supracil) faces, a 5.5-cm path length, and a volume of 60 ml. The cell is held in a bracket atop a magnetic stirrer. There was also used on occasion a Model RPR-100 Rayonet photochemical reactor with a motor-driven turntable, Model MGR-100, both from the Southern New England Ultraviolet Co.; it was used with RPR 3000-Å lamps having maximum intensity ($I_{\max}$) at 3000 Å. Photolysis tubes of Pyrex were used to remove wavelengths shorter than 3000 Å.

Emission studies were done on a spectrophotofluorimeter assembled and calibrated by Dr. R. B. Brainard[4b,62] of these laboratories. Fluorescence measurements were in spectrograde cyclopentane. Phosphorescence was studied in dried ethanol and measured phosphorescence intensities were reproducible for different samples prepared from the same solution. The recorded emission spectra were corrected by a computer program developed by R. B. Brainard.[62]

Vapor phase chromatography was done on an Aerograph A-90-P3 chromatograph with accompanying Leeds and Northrup recorder and Disc Integrator. Columns used were as follows:

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(57) The major source of difference between our rates and those of Cowan and Baum[5b] is presumably the greater exothermicity intrinsic to their system; a minor factor is the difference in k's chosen for a diffusion-controlled process.

(58) Sigal has recently published a k_{et} value of 2×10^{6} sec^{-1} for 1-phenyl-2-butene and a *higher* k_{et} of 6×10^{7} sec^{-1} for 5-phenyl-2-pentene. The former value appears to be too low to account for the absence of triplet transfer to piperylene[1] and is based on a concentration effect which we do not observe. The latter value is derived from piperylene quenching without correction for singlet quenching and using a diffusion-controlled rate constant of 1×10^{9} M^{-1} sec^{-1}, both of which factors presumably making the phenylpentene value artificially low; *cf.* C. S. Nagakawa and P. Sigal, *J. Chem. Phys.*, **52**, 3277 (1970); C. S. Nagakawa and P. Sigal, *ibid.*, **53**, 2993 (1970).

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A, 20 ft × $^{1}/_{4}$ in., 15% Carbowax 20 M; B, $2^{1}/_{4}$ ft × $^{1}/_{4}$ in., 33% $AgNO_3$–ethylene glycol; C, 5 ft × $^{1}/_{4}$ in., 5% SE-30; D, 15 ft × $^{1}/_{4}$ in., 5% Carbowax 20M; E, $3^{2}/_{3}$ ft × $^{1}/_{4}$ in., 33% $AgNO_3$–glycerol; F, 20 ft × $^{1}/_{4}$ in., 30% β,β'-oxydipropionitrile; G, 20 ft × $^{1}/_{4}$ in., 25% bis-2-(2-methoxyethoxy)ethyl ether; H, 20 ft × $^{1}/_{4}$ in., 15% azoxydianisole.[63–65] Column F was used in a Hy-Fi Model 600 chromatograph with L & N recorder and Disc Integrator.

Analysis of Photoreactions. The quantitative analysis of the cycloadduct pair from *cis*-I and unconverted phenylhexene (cis and trans) was performed on column D at 115°, using phenylcyclohexane as an internal standard. The low concentrations of materials in the photoreactions necessitated prior removal of most of the cyclopentane by passing a slow stream of nitrogen over the solution until the volume had been reduced to *ca.* 1.0 ml. Determination of cis → trans isomerization was made by isolating partially isomerized starting material using column D and analyzing for the cis–trans composition using column E at 70°. Suitable controls were performed to ensure the accuracy of these procedures. Uranyl oxalate actinometry was used throughout.[66]

***cis*-6-Phenyl-2-hexene (*cis*-I).** 6-Phenyl-2-hexyne (Chemical Samples Co., 99%) was partially hydrogenated at atmospheric pressure with 5% $Pd/BaSO_4$[67] in methanol–pyridine using H_2 either from a pressurized cylinder or generated from 1 M $NaBH_4$–1 M NaOH and glacial acetic acid in a Brown–Brown apparatus.[68] For example, 0.61 g of 5% $Pd/BaSO_4$ in 20 ml of methanol and 2.5 ml of pyridine was saturated with H_2 while magnetically stirring. After the catalyst stopped absorbing H_2, a solution of 5.02 g (31.8 mmol) of 6-phenyl-2-hexyne in 20 ml of methanol and 2.5 ml of pyridine was added and washed in with 10 ml of additional methanol. Hydrogen was absorbed rapidly but after 61 min no further uptake occurred, having absorbed 807 ml of H_2 (theoretical, for 1 equiv, 711 ml). The solution was filtered, most of the methanol was distilled away (bath 90–95°, vapor 66°), and the remaining solvent was distilled off under vacuum (bath 80°, vapor 60°, 20 mm). The residue was molecularly distilled at 80° (1 mm) to give 3.47 g (21.7 mmol, 68% yield) of *cis*-6-phenyl-2-hexene containing 1.1% trans and only traces of solvent and starting material (no detectable phenylhexane). Use of larger percentages of pyridine, up to 100%, slowed the uptake of H_2 without reducing the content of trans in the final product, nor did the use of pressure (in a Paar Hydrogenator) reduce the content of the trans isomer.

For quantitative experiments (quantum yields, quenching studies, emission studies) the material was further purified by glpc (column A) in 250-μl amounts to remove traces of solvent and 6-phenyl-2-hexyne, followed by molecular distillation under vacuum: nmr (CCl_4) δ 1.60 (3 H, broadened d, $J = 5$, CH_3), 1.7–2.3 (4 H, m), 2.65 (2 H, t, $J = 7$, benzylic CH_2), 5.49 (2 H, m, vinyl), 7.27 (5 H, s, aryl); ir (film) 3.35, 3.43, 3.53, 6.03, 6.23, 6.90, 9.74, 13.5, 14.4 μ; molecular ion *m/e* 160. *Anal.* Calcd for $C_{12}H_{16}$: C, 89.93; H, 10.07. Found: C, 89.57; H, 10.14.

***trans*-6-Phenyl-2-hexene (*trans*-I).** The Grignard coupling[69,70] of 46.3 g (0.24 mol) of β-phenylethyl bromide and 33.9 g (0.25 mol) of crotyl bromide with 6.1 g of clean, dry Mg turnings (0.24 mol) was carried out under N_2 in 70 ml of dry ether to give, after drying ($MgSO_4$) and vacuum distillation (66° (1.0 mm)), 13.4 g (0.0836 mol, 33% yield) of product composed of approximately 70% *trans*-I, 10% *cis-I*, and 20% 3-methyl-5-phenyl-1-pentene by glpc (columns A and B). No glpc conditions were satisfactory for preparative separation of *trans*-I or *cis*-I from the mixture but separation was achieved on $AgNO_3$-impregnated silica gel[71] using benzene as eluant. Chromatography of 654 mg of Grignard mixture gave three 20-ml fractions with negligible material followed by a fourth fraction containing 240 mg of 99% pure *trans*-I (1% 3-methyl-5-phenyl-1-pentene). Additional fractions gave mixtures. Further purification was accomplished by glpc on column A: nmr (CCl_4) δ 1.4–2.2 (7 H, m), 2.57 (2 H, t, $J = 7$, benzylic CH_2), 5.37 (2 H, six-line m, vinyl), and 7.08 (5 H, s, aryl); ir (film) 3.33, 3.43, 3.53, 6.25, 6.72, 6.93, 10.37, 13.42, 14.35 μ.

Anal. Calcd for $C_{12}H_{16}$: C, 89.93; H, 10.07. Found: C, 89.75; H, 10.01.

Preparation of IIa and IIb. *cis*-I (2.00 g, 0.0125 mol) was dissolved in 200 ml of cyclopentane (Burdick and Jackson spectrograde) saturated with argon and irradiated with the low-pressure mercury lamp for 3 hr to consume over 90% of starting material. The bulk of the solvent was evaporated on the rotary evaporator at 25° and the residue molecularly distilled; the material passing over at 40–87° (1.5 mm) was collected and yielded 1.55 g (0.00969 mol, 78% yield) of distillate with 0.33 g (17%) of residue. After preparative glpc of the distillate in 50-μl quantities on column A at 160° and molecular distillation (70° (1 mm)), there was obtained 0.70 g (35%) of major photoproduct II and 0.030 g (1.5%) of a minor photoproduct. II has nmr (benzene) δ 0.92, 1.06 (3 H, 2 d, $J = 7$ for both, CH_3's of 2 isomers), 1.2–2.4 (10.5 H, m), 2.84 (0.5 H, d of d, allylic), and 5.3–5.8 (2 H, vinyl); ir (film) 3.30, 3.37, 3.48, 6.29, 6.85, 6.95, 13.47 μ; molecular ion *m/e* 160.

Anal. Calcd for $C_{12}H_{16}$: C, 89.93; H, 10.07. Found: C, 89.87; H, 10.20.

II was resolved into IIa and IIb by injecting 4-μl samples on column H (134°) and collecting the trailing and leading edges of the doublet. After 59 injections, 63.6 mg of the lower retention component IIa and 63.0 mg of the second component IIb were collected with the latter being further purified by a second pass in 8–10-μl amounts. Both were freed of column bleed by passing over 5 ft × $^{1}/_{4}$ in. 30% SE-30 at 120° to give 50.9 mg of IIa (containing 10–15% IIb) and 39.6 mg of IIb (containing no detectable IIa). For IIa: ir (film) 3.29, 3.40, 3.48, 6.28, 6.86, 7.29, 7.46, 11.13, 11.74, 13.53, 14.12 μ; molecular ion *m/e* 160; uv max (cyclopentane) 213 nm (ϵ 3610, shoulder on olefinic end absorption).

Anal. Calcd for $C_{12}H_{16}$: C, 89.93; H, 10.07. Found: C, 89.66; H, 10.08.

For IIb: ir (film) 3.29, 3.40, 3.48, 6.29, 6.92, 7.29, 7.43, 11.00, 12.71, 13.35, 13.54 μ; molecular ion *m/e* 160; uv max (cyclopentane) 207 nm (ϵ 5090, shoulder on olefinic end absorption).

Anal. Calcd for $C_{12}H_{16}$: C, 89.93; H, 10.07. Found: C, 89.78; H, 10.36.

Preparation of III. *trans*-I (351 mg, 2.20 mmol) was dissolved in 200 ml of cyclopentane, saturated with argon, and irradiated with the low-pressure mercury lamp for 100 min (85% conversion). Most of the solvent was removed in the rotary evaporator at 25° and the residue molecularly distilled under vacuum. Analysis of the product by glpc (column A, 165°) showed a single major product (70%, retention time relative to starting *trans*-I, 0.81) along with two minor photoproducts (9%, 0.64, and 7%, 0.95) and 14% (0.75) *cis*-I photocycloadduct mixture. Collection of the major photoproduct was complicated by the similar retention time of the *cis*-I photocycloadduct, but was accomplished in two passes to yield 68 mg (0.425 mmol) of 99% III: ir (film) 3.29, 3.33, 3.36, 3.47, 6.27, 6.94, 7.31, 7.43, 10.82, 13.22, 14.01 μ.

Anal. Calcd for $C_{12}H_{16}$: C, 89.93; H, 10.07. Found: C, 89.64; H, 10.12.

Pyrolysis of II. II undergoes thermal rearrangement at temperatures above 330° in the injection port of a gas chromatograph to produce a merged double peak of shorter retention time on column A. Considerable experimentation established that the most efficient method of preparative thermolysis was to inject 6-μl samples repeatedly and consecutively with the injector at 370° and column at 170° until about 200 mg accumulated in a collection device left in the collector port throughout. The condensate was freed of unconverted starting material by a second pass in 25-μl amounts to produce 130 mg of thermolysis mixture. The mixture was injected in 6-μl amounts on column A at 108° to collect 37.5 mg (0.234 mmol) of the shorter retention component IXb and 42.0 mg (0.262 mmol) of the second isomer IXa, each containing about 5% of the other isomer. Thermolysis of samples of the individual *cis*-I photocycloadducts under the same conditions, either alone or admixed with II, established that IIa converts solely to IXa while IIb converts solely to IXb. Both show only olefinic end absorption in the uv (no absorption above 225 nm) and molecular ions at *m/e* 160: nmr (CCl_4) IXa, δ 1.05 (d, $J = 7$ Hz, 3, methyl), 2.2 (m, 7, methylene chain and H-6), 2.52 (m, $J = 15.8, 8.5$ Hz + fine splitting, 1, H-4 exo), 2.8 (m, 2, H-4 endo and H-5), 3.48 (bd, $J = 8.8$ Hz, 1, H), 5.6 (m, 2, H-2 and H-3); IXb, 1.6 (m, 9, methylene chain and

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methyl), 2.40 (m, J = 16.8 Hz, 1, H-4 exo), 2.6 (m, 2, H-4 endo and H-6), 3.24 (m, 1, H-1), 5.21 (m, 1, H-8), 5.5 (m, 2, H-2 and H-3).

Anal. Calcd for $C_{12}H_{16}$ (for IXa): C, 89.93; H, 10.07. Found: C, 89.87; H, 10.14.

Peracid Titration of II.[72] A solution of dry ethereal monoperphthalic acid (0.160 N) was prepared and 2.00-ml aliquots treated with II for (a) 3 hr at 25°, (b) overnight at −5°, and (c) 14 days at −5°. Titration of unreacted peracid with 0.05 N $Na_2S_2O_3$ after addition of excess potassium iodide solution gave 0.89, 1.02, and 1.04 peracid equiv for the three sets of conditions.

Hydrogenation of II in Benzene. Tetrahydro II. A slurry of 15 mg of 10% Pd/C in 1 ml of benzene was saturated with H_2 in a microhydrogenation vessel and 53.2 mg (0.332 mmol) of II in 1 ml of benzene was added. After 90 min, 13.9 ml of H_2 (0.564 mmol, 1.71 equiv) was absorbed. Conversion by glpc (column A) was 90%. The products were collected by glpc (column A) and the mass spectrum showed a molecular ion at m/e 164 (no peaks at m/e 160 and 162).

Anal. Calcd for $C_{12}H_{20}$: C, 87.73; H, 12.27. Found: C, 87.85; H, 12.16.

Hydrogenation of II in *tert*-Butylamine and *n*-Hexane. Dihydro II.[73] Pd/C (10%; 25.2 mg) in 0.50 ml of *n*-hexane plus 390 mg (5.34 mmol) of *tert*-butylamine were saturated with H_2 and cooled to 0° in a microhydrogenation vessel while magnetically stirring. II (280 mg, 1.75 mmol) in 1.0 ml of *n*-hexane was added and after 77 min no further uptake occurred, having absorbed 41.7 ml of H_2 (1.71 mmol at standard temperature and pressure, 0.98 equiv). The solution was filtered, concentrated with a stream of N_2, and examined by glpc (column A) which showed two well-merged peaks at shorter retention than II. The double peak was collected (192 mg, 1.20 mmol, 69%). The spectral data confirmed that the olefinic function was no longer present and that no tetrahydrogenated material was present: nmr (CCl_4) δ 0.84, 1.04, (3.6 H, 2 d, J = 7 for both, CH_3's of two isomers) and 0.8–2.3 (14.4 H, m); ir (film) 3.34, 3.45, 6.86, 6.94, 7.31 μ; molecular ion m/e 162 (no peaks at m/e 160 or 164).

Anal. Calcd for $C_{12}H_{18}$: C, 88.82; H, 11.18. Found: C, 88.52; H, 11.29.

Turntable Experiments. All samples for the turntable experiments were prepared in a similar manner. Vycor photolysis tubes were filled with about 52 ml of solvent (cyclopentane, except in triplet-counting experiments) and reactants weighed into each, liquids being measured by weighing a syringe before and after dispensing into the tube. A slow stream of argon (or O_2 in certain experiments) was bubbled through each of the tubes using clean 2 mm o.d. glass tubes for about 1 hr; each was sealed with a rubber stopple immediately after the delivery tube was withdrawn. Volatile sensitizers or quenchers (acetone, *cis*-piperylene) were injected through the rubber stopple, weighing the syringe before and after delivery, and each tube was adjusted to the etched 50.0-ml mark by injecting solvent (separately saturated with argon), taking care in both cases to exclude air bubbles from the syringes. The tubes were placed in one of the turntables (which were shown to expose equal segments of the tubes to the light) and irradiated with the low-pressure mercury lamp. After photolysis an internal standard was added to the required tubes and analysis of the samples, concentrated by a stream of N_2, was performed as described above, except for the triplet-counting experiments where the isomerization of *cis*-piperylene was measured without internal standard or concentration of the reaction mixture. Because of space limitations, detailed results of the quantum efficiency, quenching, oxygen effect, and triplet counting experiments have had to be eliminated from this section. The appropriate tables may be found in the doctoral dissertation of W. F.[2]

Wavelength Dependence of Formation of II. The monochromator with uv grating was used for the photolysis of *cis*-I in solutions concentrated enough (13 mM) to absorb 99.9% of the light at even the lowest extinction wavelength limits used (238 and 270 nm), and even greater absorption at intermediate wavelengths. The solutions, contained in the water-jacketed cell maintained at 15–19° by a slow stream of tap water, were saturated with argon and stoppered just prior to irradiation. Light intensities were determined before and after irradiation (for an average) by uranyl oxalate actinometry using solutions 0.3 times as concentrated as normal to shorten irradiation times. The slits on the monochromator were set at 4.3 mm (entrance) and 2.5 mm (exit) to give a total dispersion of 8.0 nm. The data are presented in Table VI.

Table VI. Wavelength Dependence for Formation of II[a]

Excitation wavelength, nm	*cis*-I, mg	Measured light intensity[b] Before	Measured light intensity[b] After	Hr irrad	II, mg
262 ± 8	125.5	7.0	8.0	50.1	0.553
246 ± 8	122.8	36	40	18.7	2.48

[a] Temperatures of first and second actinometers and the reaction mixture were (262-nm photolysis) 17.0, 18.6, and 15.5°, respectively, and (246-nm photolysis) 16.1, 16.5, and 15.0°, respectively. The quantum yields of the actinometer were corrected for the small temperature coefficients, using 0.57 at 262 nm and 0.60 at 246 nm. Analysis was performed on column D. Concentration of *cis*-I = 13.1 and 12.7 mM, respectively. [b] Units of 10^{13} $h\nu$/sec.

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