# Photochemistry of Bichromophoric Molecules. Internal Photocycloaddition of 6-Phenyl-2-hexyne[1,2]

Wolfgang Lippke, William Ferree, Jr., and Harry Morrison*

Contribution from the Department of Chemistry, Purdue University, West Lafayette, Indiana 47907. Received September 18, 1973

Abstract: Photolysis of the title compound in hexane solution using 254-nm light leads to the formation of a cyclooctatetraene (A), 2-methylbicyclo[6.3.0]undeca-1,3,5,7-tetraene. The quantum efficiency is 2.6×10^{-3}, some 100-fold less than was observed for 6-phenyl-2-hexene. It is found that *trans*-2-heptene has a negligible quenching effect on the cycloaddition, yet its isomerization is effectively sensitized by the phenyl triplets of the arylhexyne. It is concluded that internal cycloaddition of the acetylene moiety to the benzene ring proceeds *via* the phenyl excited singlet state.

The photochemistry of bichromophoric molecules continues to be a subject of considerable interest,[3] representing, as it does, a logical extension of the vast amount of research historically devoted to monochromophoric compounds. As part of our own program in this area, we have had occasion to study the photochemical and photophysical properties of several nonconjugated aryl olefins, *i.e.*, 1-phenyl-2-butene,[4] 6-phenyl-2-hexene,[5] and 2-methylenebenznorbornene.[6] The arylhexene is a particularly interesting molecule, with irradiation leading predominantly to internal cycloaddition ($\phi_{254} = 0.26$) accompanied by less efficient ($\phi_{254} = 0.01$) cis $\rightleftarrows$ trans isomerization of the olefin (eq 1). The photophysical properties of the
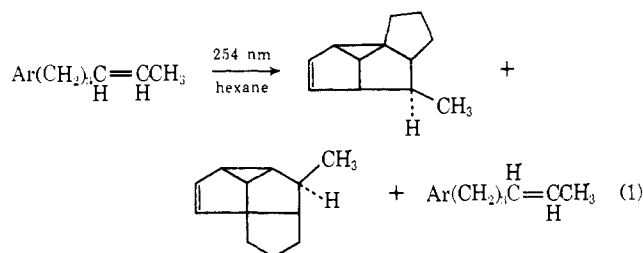
molecule (inefficient fluorescence, shortened singlet lifetime, few detectable phenyl triplets) and the results of quenching studies led us to propose that excitation of 6-phenyl-2-hexene results in very rapid intramolecular singlet exciplex formation, followed, in part, by internal cycloaddition.[7] We suggested[8] that the photophysical properties of 6-phenyl-2-hexene (with its two nonidentical chromophores) were analogous to the spectroscopic observations made with diphenylalkanes[9] (whereby

separation by three carbons leads to rapid singlet excimer formation). Our own observations of photochemistry resulting from rapid internal complexation of a singlet species were extended to the 5-hepten-2-one molecule[3b] and a number of related observations[3a,10] further attest to the widespread photochemical significance of this phenomenon.[11]

During the course of our research with 6-phenyl-2-hexene, it was noted that 6-phenyl-2-hexyne also exhibited a reduction in ϕ_f relative to the saturated analog, a reduction not so striking as with the aryl olefin but yet significant. Since the greatly diminished fluorescence of 6-phenyl-2-hexene seemed to be coupled with its propensity for efficient internal cycloaddition, and since photocycloaddition of acetylenes to benzenoid aromatics has been reported (see Discussion), it seemed reasonable that the reduction in ϕ_f might be photochemically significant. The results of our subsequent studies are described below.

Results

A. Photolysis of 6-Phenyl-2-hexyne. Identification of the Photoisomer (A). Irradiation of a *ca.* 0.03 *M* solution of the arylacetylene in argon degassed cyclopentane, using 254-nm light, results in the inefficient formation of one major photoproduct (A) detectable by vpc. A was isolated as a pale yellow oil, either by vpc or by extraction into an aqueous silver nitrate solution. It analyzed as an isomer, $C_{12}H_{14}$, with a molecular ion at m/e 158. The benzenoid absorption of the starting material is completely absent in the nmr, there now being a methyl singlet at δ 1.75, multiplets at δ 1.97 (2 H) and 2.38 (4 H) corresponding to two

(1) Organic Photochemistry, part XXVII. Part XXVI: P. Froehlich and H. Morrison, *J. Amer. Chem. Soc.*, **96**, 332 (1974).

(2) Abstracted from the Masters Thesis of W. Lippke, Purdue University, May, 1973.

(3) (a) For a recent review, see F. C. De Schryver and J. Put, *Ind. Chim. Belge*, **37**, 1107 (1972); (b) S. R. Kurowsky and H. Morrison, *J. Amer. Chem. Soc.*, **94**, 507 (1972), and references therein.

(4) H. Morrison and R. Peiffer, *J. Amer. Chem. Soc.*, **90**, 3428 (1968); H. Morrison, J. Pajak, and R. Peiffer, *ibid.*, **93**, 3978 (1971).

(5) W. Ferree, Jr., J. B. Grutzner, and H. Morrison, *J. Amer. Chem. Soc.*, **93**, 5502 (1971).

(6) F. Scully, J. Grutzner, and H. Morrison, *J. Amer. Chem. Soc.*, **95**, 5100 (1973).

(7) A previously observed[5] wavelength effect, whereby the quantum efficiency of cycloaddition increased on the high frequency side of the B_{2u} band, has not been reproducible and now seems to have been an artifact apparently caused by a defective grating.

(8) H. Morrison and W. Ferree, Jr., *J. Chem. Soc., Chem. Commun.*, 268 (1969).

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

(10) N. J. Leonard, K. Golankiewicz, R. S. McCredie, S. M. Johnson, and I. C. Paul, *J. Amer. Chem. Soc.*, **91**, 5855 (1969); E. A. Chandross and C. J. Dempster, *ibid.*, **92**, 703 (1970); D. G. Whitten and W. E. Punch, *Mol. Photochem.*, **2**, 77 (1970); P. J. Wagner, P. A. Kelso, A. E. Kempainnen, A. Hang, and D. R. Graver, *ibid.*, **2**, 81 (1970); F. R. Stermitz, D. E. Nicodem, V. P. Muralidharan, and C. M. O'Donnel, *ibid.*, **2**, 87 (1970); D. R. G. Brimage and R. S. Davidson, *J. Chem. Soc., Chem. Commun.*, 1385 (1971); J. Rennert, S. Soloway, I. Waltcher, and B. Leong, *J. Amer. Chem. Soc.*, **94**, 7242 (1972) (a singlet complex is likely here but has not been proposed); J. Put and F. C. deSchryver, *ibid.*, **95**, 137 (1973), and references therein; E. A. Chandross and A. H. Schiebel, *ibid.*, **95**, 611 (1973).

(11) The rapid intramolecular interaction characteristic of these small aliphatic chains (*cf.* the "$n = 3$ rule")[3a,5,8] is of course not restricted to the electronically excited state. Some interesting nonphotochemical studies are M. Itoh and E. M. Kosower, *J. Amer. Chem. Soc.*, **90**, 1843 (1968); M. Itoh, *ibid.*, **93**, 4750 (1971); M. Itoh, *ibid.*, **94**, 1034 (1972); J. St. Denis, T. Dolzine, and J. P. Oliver, *ibid.*, **94**, 8260 (1972); P. Caluwe, K. Shimada, and M. Szwarc, *ibid.*, **95**, 1433 (1973).

allylic and one more shielded methylene groups, and three singlets at δ 5.54 (1 H), 5.64 (2 H) and 5.75 (2 H). These nmr data are comparable with those reported[12] for the cyclohexyl fused cyclooctatetraene (bicyclo-[6.4.0]dodeca-1,3,5,7-tetraene), in which the methylene hydrogens appear between δ 1.5 and 2.5 and the vinyl region consists of a "multiplet" between δ 5.50 and 5.90. The uv spectra of the two compounds also match closely, with A having a small peak superimposed on rising end absorption, λ_{max} 288 nm (ϵ 282); the cyclohexyl fused derivative has a shoulder at 280 nm (ϵ 290). These data, and the logical maintenance of a vicinal relationship between the five-membered ring and the methyl group, allow for the assignment of A as 2-methylbicyclo[6.3.0]undeca-1,3,5,7-tetraene, there being no possible distinction between the two bond switch tautomers on the basis of data in hand.[13]

and/or

CH₃   CH₃
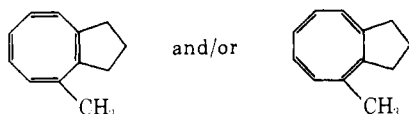
B. Quantum Efficiency for Formation of A (ϕ_{app}). The quantum efficiency for formation of A is 3.3 × 10⁻³ (av of four determinations using ∼2 × 10⁻² M solution in hexane). As anticipated from the observation of high boiling polymeric side products,[13] the formation of A represents only a portion (ca. 13%) of the quantum efficiency for disappearance of starting material; a study of this fraction as a function of 6-phenyl-2-hexyne concentration showed the anticipated increase upon dilution i.e., at 0.5 × 10⁻² M, formation of A accounts for 28% of the loss of starting material. The ϕ_{app} values are sensitive to percentage conversion to A, the product being an efficient quencher of the cycloaddition (the ϕ_{app} value was determined in experiments involving conversions of ∼3%).

C. Quenching Experiments. 1. *trans*-2-Heptene. This olefin has been useful in triplet counting experiments (see below) and is a reasonably efficient quencher of the benzenoid triplet state (the rate constant of triplet energy transfer from benzene to 2-octene has been estimated[14] to be 3.4 × 10⁹ M⁻¹ sec⁻¹, i.e., 34% of the diffusion-controlled value). In fact, addition of *trans*-2-heptene had only a negligible effect on the formation of A. Values of ϕ^0/ϕ obtained for three different heptene concentrations are 1.00 (0.1 M), 1.02 (0.2 M), and 0.98, 1.08 (0.3 M); these values are of the order of magnitude observed for the (highly inefficient) fluorescence quenching caused by 2-heptene.

2. Cyclooctatetraene (COT). Cycloaddition of cyclooctyne to benzene has been reported to be subject to quenching by COT.[15] As was observed for the intermolecular reaction[15] we found that conversion to A was reduced with increased photolysis time (thereby making isolation of appreciable amounts of A quite tedious) and COT itself proved to be an efficient quencher of the reaction. The Stern–Volmer slope is 300.2 ± 32.6 M⁻¹

(12) L. A. Paquette, R. H. Meisinger, and R. E. Wingard, Jr., *J. Amer. Chem. Soc.*, **95**, 2230 (1973).

(13) In addition to A, an intractable oil could be isolated from all photolyses, which gave an ion in the mass spectrum corresponding to twice the monomer molecular weight. All attempts to purify this material were without success.

(14) R. R. Hentz and R. M. Thibault, *J. Phys. Chem.*, **77**, 1105 (1973).

(15) R. D. Miller and V. Y. Abraitys, *Tetrahedron Lett.*, 891 (1971).
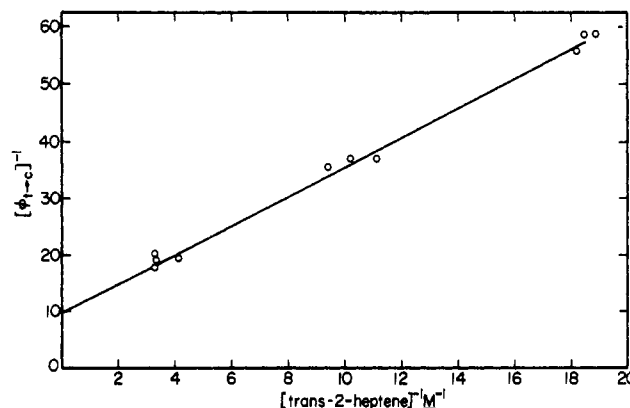

Figure 1. 6-Phenyl-2-hexyne photosensitized isomerization of *trans*-2-heptene as a function of olefin concentration.

after correction for competitive light absorption by the COT. These data stand in marked contrast to those obtained with the relatively efficient triplet quencher, 2-heptene (see above), and this fact coupled with a consideration of the extensive overlap between alkylbenzene fluorescence (λ_{max} ∼280 nm) and COT absorption strongly implicates a long range singlet energy transfer mechanism[16] for COT quenching.

3. Oxygen. Photolysis of 20 mM 6-phenyl-2-hexyne in oxygen saturated *n*-hexane results in the complete elimination of A. However, there is a concomitant increase in the loss of starting material relative to a degassed sample and this fact vitiates any conclusions one can draw.

D. Triplet Counting. 1. 6-Phenyl-2-hexyne. It is now well established that simple olefins are preferable to dienes for chemical triplet counting of benzenoid aromatics.[5,14,17] This is because dienes such as piperylene are good singlet quenchers, isomerize with moderate efficiency on direct irradiation, and have an appreciable extinction coefficient at 254 nm. We thus studied the sensitized isomerization of *trans*-2-heptene as a function of olefin concentration and obtained the data shown in Figure 1. These data have been corrected for the small amount of singlet quenching by the olefin (see below) and conversions to *cis*-2-heptene were kept sufficiently low (ca. 2%) so as to make back reaction corrections unnecessary. The plot corresponds to the expression

$$\frac{1}{\phi_{t \to c}} = \frac{1}{\phi_{isc}\alpha} + \frac{1}{\phi_{isc}\alpha k_q \tau[Q]}$$

where $\alpha = k_c/(k_c + k_t)$. The least-squares derived intercept is 10.3, so that using $k_c/(k_c + k_t) = 0.50$ (see below), ϕ_{isc} for 6-phenyl-2-hexyne is calculated as 0.19.

2. 1-Phenylhexane. For purposes of comparison, triplet counting experiments were also done on this monochromophoric analog of the aryl–acetylene system. A slightly different approach was employed, with both the *cis*- and *trans*-2-heptenes separately used as quenchers. Only two different olefin concentrations were used in each case (ca. 0.05 and 0.30 M), and since there was

(16) A. Lamola in "Energy Transfer and Organic Photochemistry," P. Leermakers and A. Weissberger, Ed., Interscience, New York, N. Y., 1969.

(17) F. A. Carroll and F. H. Quina, *J. Amer. Chem. Soc.*, **94**, 6246 (1972).

no appreciable concentration dependency evident in either direction,[18] the data (corrected for back reaction and fluorescence quenching) are averaged to give $\phi_{c \to t} = 0.17$ and $\phi_{t \to c} = 0.18$. Assuming complete energy transfer,[18] $\phi_{isc} = \phi_{c \to t} + \phi_{t \to c} = 0.35$. This value compares well with the 0.38 previously obtained using cis-piperylene[5] and the value of 0.42 recently reported for toluene.[14] It should be noted that all these values are considerably lower than the ϕ_{isc} of 0.52 recently communicated for toluene,[17] a particularly bothersome point considering the rigorous degassing techniques employed by Hentz and Thibault,[14] which should have provided a comparably higher value if lack of efficient transfer were the sole problem.[18]

In any event, the ability of 2-heptene to intercept phenylhexyne triplets and the appreciable decrease of ϕ_{isc} in this molecule by comparison with phenylhexane are both indisputable.

E. Spectroscopic Properties of 6-Phenyl-2-hexyne. The benzene B_{2u} bands for 1-phenylhexane and 6-phenyl-2-hexyne are essentially identical in position and intensity, and, as with the 6-phenyl-2-hexene,[5] there is no evidence of a significant perturbation of this low-lying, photochemically active, excited singlet state. The fluorescence emission spectra of the two molecules at room temperature are likewise identical in peak position, but ϕ_f for the acetylene is only 83% of the saturated analog (i.e., 0.10). At 77°K (using isopentane), the total emission of the phenylhexyne is also 83% of the arylhexane, with the ϕ_f/ϕ_p ratios of the two molecules being comparable (2.1 vs. 2.4). Peak positions, shape, and fine structure of the two substrates' fluorescence and phosphorescence emission are essentially identical.

trans-2-Heptene had a slight quenching effect on the fluorescence emission of 6-phenyl-2-hexyne. Using a substrate concentration of 23 mM, ϕ_f^0/ϕ_f values at various heptene concentrations were 1.06 (0.044 M), 1.12 (0.090 M), 1.19 (0.300 M), and 1.23 (0.634 M).

Discussion

It is thus clear that 6-phenyl-2-hexyne does indeed resemble the previously observed photochemistry of 6-phenyl-2-hexene, in that internal cycloaddition occurs (eq 2), although some 100-fold less efficiently. As was the case with the aryl olefin, this reaction is an *intramolecular* analog of previously reported *intermolecular* cycloadditions. These latter include the addition to benzene of dimethyl acetylenedicarboxylate,[21,22] methyl propiolate,[22] phenylacetylene,[22] perfluoro-2-butyne,[23]

cyclooctyne,[16] and acetylene itself.[24] In all cases, a cyclooctatetraene is the final product.

$$Ar(CH_2)_3C\equiv CCH_3 \xrightarrow[\text{hexene}]{254 \text{ nm}} \quad \text{(2)}$$
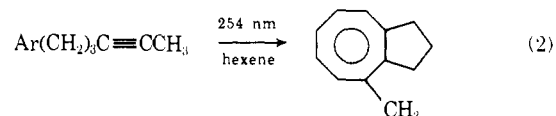
If one assumes 6-phenyl-2-hexyne can be treated as a pair of isolated chromophores (and the absorption spectrum supports such an assumption), the primary question is to which phenyl excited state does the acetylene add? As was the case for the aryl olefin system, the above cited studies of the intermolecular reactions are not very informative on this point. Miller and Abraitys[16] imply a triplet precursor for the cyclooctyne cycloaddition in that COT quenching is reported and it is noted that COT is known to be a triplet quencher. However, we, for reasons discussed in the Results section, are convinced that such quenching, at least as it pertains to our system, must be attributed to singlet–singlet energy transfer.[25]

On the other hand, we have elsewhere presented arguments in favor of the benzene excited singlet as the precursor for olefin cycloaddition. The results of experiments involving trans-2-heptene in the present case support a similar conclusion for acetylenes. In particular, trans-2-heptene is incapable of quenching formation of the cyclooctatetraene even while it effectively intercepts 6-phenyl-2-hexyne triplets. *This can only be interpreted to mean that the phenyl triplet is not on the reaction path leading to the cycloadduct and that the phenyl excited singlet state is the reactive species.* It is of interest that a naphthalene excited singlet state has been proposed as the reactive species for diphenylacetylene cycloaddition to that molecule.[26,27] As regards the question of which valence bond isomer(s) precedes the eventual formation of the cyclooctatetraene, one can write plausible mechanistic schemes involving (1,2), (1,3), or (1,4) internal cycloaddition to the benzene ring. We have no evidence which bears on this point[28] but, in at least one case,[24] a 1,2 cycloadduct has been trapped (with tetracyanoethylene) and evidence against 1,3 cycloaddition is presented.

(18) No obvious trend could be discerned in the c → t data; there is a suggestion of a small concentration dependence for the t → c values. The extrapolated value for $\phi_{t \to c}$ at infinite olefin concentration is 0.21, the use of which would raise ϕ_{isc} to 0.38.[19]

(19) The difference between the ϕ_{isc}'s, i.e., 0.35 and 0.38, is small and comparable to the experimental error. However, the larger deviation of $\phi_{t \to c}/\phi_{c \to t}$ from unity, if real, implies that the decay ratio (k_c/k_t) for olefin triplets produced by alkylbenzenes is likewise not exactly unity (it is unity for benzene[20]). Further study of this point is clearly warranted since an assumption of unity is presently commonplace[14] but not well substantiated. It may be worth recalling in this context that the photostationary state, and thus the excitation ratio for the toluene–2-heptene system, very definitely does deviate markedly from unity (again by contrast with benzene).[4]

(20) M. A. Golub and C. L. Stephens, J. Phys. Chem., 70, 3576 (1966).

(21) E. Grovenstein and D. Rao, Tetrahedron Lett., 148 (1961); E. Grovenstein, T. C. Campbell, and T. Shibata, J. Org. Chem., 34, 2418 (1969).

(22) D. Bryce-Smith and J. E. Lodge, Proc. Chem. Soc., London, 333 (1961); D. Bryce-Smith and J. E. Lodge, J. Chem. Soc., 695 (1963).

(23) R. S. H. Liu and C. G. Krespan, J. Org. Chem., 34, 1271 (1969).

(24) D. Bryce-Smith, A. Gilbert, and J. Grzonka, J. Chem. Soc., Chem. Commun., 498 (1970).

(25) Though the site of excitation in our molecule is unequivocal, excitation of the acetylene moiety by direct irradiation[24] or sensitization[15] has been suggested. The latter observation in particular is curious, since energy transfer from acetone to the cyclooctyne is proposed; it is clear that at least in the simple acyclic system such transfer would be highly endothermic (compare, for example, the considerable phosphorescence observed for 6-phenyl-2-hexyne with the total lack of phosphorescence characteristic of 6-phenyl-2-hexene).

(26) R. J. McDonald and B. K. Selinger, Tetrahedron Lett., 4791 (1968); W. H. F. Sasse, P. J. Collin, D. B. Roberts, and G. Sugowdz, Aust. J. Chem., 24, 2151 (1971).

(27) The olefin–benzene and tolan–naphthalene cycloadditions have been proposed as proceeding via a singlet exciplex.[5,26] The data in the present case are somewhat ambiguous. It is true that the fluorescence efficiency is reduced at room temperature and increases somewhat (relative to phenylhexane) at 77°K. Both observations mirror that observed for molecules in which internal complexation is occurring.[5] However, singlet lifetime studies have not given any consistent evidence of a reduced lifetime for the aryl–acetylene, and the reduced ϕ_{isc} value of this molecule could conceivably be caused, at least in part, by singlet quenching by-products.

(28) We have tried unsuccessfully to find spectrophotometric evidence of an intermediate by irradiation at 77°K. We thank Professor E. Fischer of the Weizmann Institute for allowing us to use his facilities for this experiment.

Experimental Section

Instrumentation and Materials. Infrared spectra were recorded on a Beckman IR-8 spectrometer; uv spectra were recorded either on a Cary 15 recording spectrometer or on a Gilford photometer (Model 222A) coupled to a Beckman DU monochromator; nmr spectra were obtained in a Varian A-60A or a Varian XL-100 spectrometer; mass spectra were recorded with a Hitachi RMU-6A mass spectrometer. Emission spectra were recorded on a previously described[29] home-made fluorometer and are corrected for photomultiplier response;[30] a low-pressure mercury lamp was the source.

A Hanovia low-pressure mercury resonance lamp (688A-45) emitting at 253.7 nm was used for the preparative photolyses and turntable experiments. Vycor test tubes sealed by rubber stopples were placed in a water bath maintained at 17°. Wavelength experiments were done using a Bausch and Lomb high intensity monochromator as previously described.[5] Uranyl oxalate actinometry was employed throughout. Vapor phase chromatography was done using a Varian Aerograph A-90P (preparative) or series 1400 (analytical) instrument, both associated with Disc Integrators. Columns were as follows: (A) 10 ft × $^1/_8$ in., 3% Carbowax 20M; (D) 20 ft × 0.25 in., 25% Carbowax 1540; (E) 20 ft × $^1/_8$ in., 30% β,β'-oxydipropionitrile, all on 60-80 mesh Chromosorb W, acid washed, DMCS treated. Quantitative analyses were done using an internal standard, phenylcyclohexane, with response factors for 6-phenyl-2-hexyne and the photoproduct equal to 0.892 ± 0.006 and 0.864 ± 0.004, respectively.

6-Phenyl-2-hexyne (99%, vpc pure), cyclooctatetraene (99%, vpc pure), and *trans*-2-heptene (99%, 100% trans by vpc) were from Chemical Samples Co.; *cis*-2-heptene (96.8% cis by vpc) was from K & K; phenylcyclohexane was from Eastman Chemical Co.; and 1-phenylhexane was from Matheson Coleman and Bell. All were molecularly distilled before use. Cyclopentane, hexane, and pentane were Burdick and Jackson "Distilled in Glass" and were transparent in the uv above 240 nm; isopentane (99.5%, Phillips Instrument Grade) was purified by one pass through a 100-g silica gel column.

Preparation of "A." After degassing for 1 hr with argon, a solution of 970 mg of 6-phenyl-2-hexyne in 220 ml of pentane was irradiated under an argon atmosphere with the low-pressure mercury lamp for 8 hr. The solvent was removed on a rotary evaporator and molecularly distilled to yield, at 45-105° (1.0 mm), 560 mg. Purification by vpc on column D at 200° gave 48 mg of A as a yellow oil: ir (film) 3.31, 3.40, 3.51, 6.15, 7.00, 7.32, 8.25, 11.6, 12.3, 13.05, 14.0 μ; molecular ion m/e 158; nmr (CDCl$_3$) δ 1.75 (3 H, singlet), 1.97 (2 H, multiplet) 2.38 (4 H, multiplet), 5.54, 5.64, and 5.75 (5 H, 2:2:1 ratio); uv$_{max}$ (hexane) 288 nm (log ϵ = 2.45).

Anal. Calcd for C$_{12}$H$_{14}$: C, 91.09; H, 8.91. Found: C, 90.91; H, 8.96.

(29) R. Brainard and H. Morrison, *J. Amer. Chem. Soc.*, **93**, 2685 (1971).

(30) R. Brainard, Ph.D. Thesis, Purdue University, August, 1970.

An alternative procedure for isolation of A was to extract 50-ml portions of the photolysis mixture with five 50-ml portions of 20% aqueous silver nitrate. The combined aqueous layers were poured onto a mixture of concentrated ammonium hydroxide and ice and reextracted with hexane. The hexane was dried, concentrated to 25 ml, and passed through a 10-g silica gel layer in a sintered glass funnel. The silica was washed with 400 ml of cyclopentane and the solvent evaporated to give the cycloadduct.

Quantum efficiency experiments were carried out in vycor tubes using *n*-hexane as solvent. The tubes were degassed for 1 hr with argon, capped with rubber stopples placed in a turntable, and irradiated with a low-pressure mercury lamp for 8 hr. Actinometer tubes were run before and after sample photolysis. Phenylcyclohexane was added to the tubes as an internal standard and analyses were performed with column A. Using a column temperature of 128°, injector temperature at 200°, detector temperature at 230°, nitrogen flow = 30 ml/min, hydrogen flow = 30 ml/min, air flow = 300 ml/min, retention times were A 7 min, standard 9.5 min, starting material 17 min. In one run, 5.55 and 5.25 mg of product were produced in separate tubes with a light intensity of 1.85 × 10^{17} $h\nu$/sec. In a second run, 4.41 and 4.24 mg of product were formed with a light intensity of 2.09 × 10^{17} $h\nu$/sec. Starting material concentrations were *ca.* 2 × 10^{-2} M. For quantum efficiencies of disappearance, the 6-phenyl-2-hexyne was added by syringe through the stopple after degassing, so as to prevent loss of starting material by evaporation.

Quenching and Triplet Counting Experiments. These were carried out in a turntable using vycor tubes and the general procedure described above. The oxygen experiment was done by saturating a tube with pure oxygen. For the triplet counting data, analyses of the heptene isomers were done on column E with the column temperature at 200°, injector temperature at 200°, detector temperature at 200°, and nitrogen, hydrogen, and air flows as described above for column A. Under these conditions, *trans*-2-heptene has a retention time of 15.5 min and *cis*-2-heptene at 18 min. Analyses were done either by relating the areas of the two isomers or by the use of an internal standard (cyclohexane). The use of an internal standard allowed the confirmation of no loss of olefin during the experiment.

Emission Spectroscopy. Fluorescence spectra were done on *ca.* 6 × 10^{-3} M solutions in hexane, degassed with argon for 12 min, at 27°. Spectra were corrected for relative absorbancies at 254 nm. Total emission spectra were done on samples with absorbances at 4-mm path length = 0.05-0.10, using 8 freeze-pump-thaw cycles at less than 1 μ for degassing. All emission data have been corrected and the areas calculated by previously described computer programs.[30]