

were corrected for refractive index and for slight differences in absorbance.²³

Determination of Relative Quantum Yields of 2 and 3. Three samples were prepared such that the concentration of **1** was $5.9 \times 10^{-3} M$. The solvent in the first sample was pure benzene. The sample was degassed and irradiated for 12 hr at which time starting material was completely reacted. The ratio of **3** to **2** was 1:22 (by nmr). The solvent for the second sample was 2.48 *M* bromocyclopropane in benzene. After degassing and irradiating for 12 hr, no starting material remained, and the only detectable product was **2**. A sample with benzene as solvent was saturated with oxygen and irradiated for 22 hr. In this case, the only detectable compound was starting material **1**.

Determination of Quantum Yields for Disappearance of 1. The ferrioxalate method was used²⁴ for actinometry, and the concentration of **1** was measured spectrophotometrically at 345 nm. The concentration of **1** in all runs was sufficient to absorb 99% of the incidental light.

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Photochemical Heavy-Atom Effect. V. Reaction of Acenaphthylene with *cis*- and *trans*-1,3-Pentadiene

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Abstract: The heavy-atom solvent dibromomethane facilitates the cross cycloaddition of acenaphthylene (**1**) to *cis*-1,3-pentadiene (**3**) in a regioselective and stereoselective manner to produce *syn*-6-(*cis*-1-propenyl)[1',8']naphthobicyclo[3.2.0]hept-2-ene (**5d**) and the corresponding anti-*cis* isomer **5b** as 90% of the product mixture. Similarly, **1** adds to *trans*-1,3-pentadiene (**4**) to produce in over 90% of the total product mixture *anti*-6-(*trans*-1-propenyl)[1',8']naphthobicyclo[3.2.0]hept-2-ene (**5a**) and the corresponding *syn*-*trans* isomer (**5c**). The reaction of **1** with **3** or **4** is sensitized by the dye Rose Bengal to give product ratios similar to those found in the direct irradiation studies. The reaction of **1** with **3** or **4** is quenched efficiently by saturated oxygen solutions. These results verify the excited triplet state of **1** as the reactive species. Kinetic parameters are derived from a concentration study of the reaction of **1** with **3**. The stereochemical and kinetic evidence is interpreted as supporting the intervention of a triplet diradical intermediate in the cycloaddition reactions.

The genesis of cross cycloaddition reactions to acenaphthylene (**1**) evolved from the discovery by Cowan and Drisko² that the photodimerization of **1** was beneficially perturbed when heavy atom solvents were present. We undertook an extensive study of the heavy atom effect (HAE) and reported that **1** undergoes photochemical cycloaddition to a variety of substrates in the presence of heavy atom solvents.³ Other investigators have also reported similar results.⁴

An interesting result emerged from the study of the photoaddition of **1** to cyclopentadiene (**2**).^{3a} The excited triplet state of **1** adds to **2** in an inefficient manner that suggests the presence of an energy-wasting step in the reaction mechanism. Some reversibly formed species appears to be involved. It may be a triplet exciplex between **1** and **2** or an

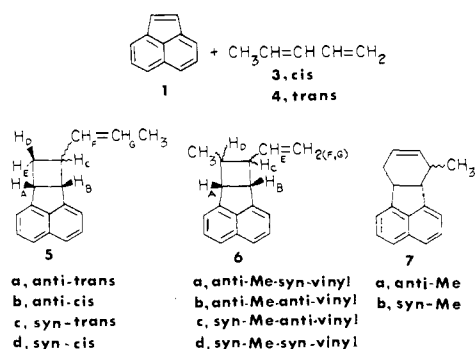
intermediate diradical.

We have investigated with the use of the HAE the photoaddition of **1** to *cis*-1,3-pentadiene (**3**) and *trans*-1,3-pentadiene (**4**) to see if additional data might cast light on the adumbrative exciplex. The results of this investigation form the basis for this report.

Results

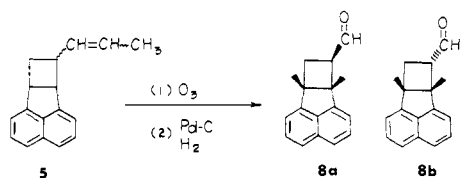
Structure of Products. Chart 1 illustrates the product structures that have been identified as arising from a photochemical reaction between **1** and **3** or **1** and **4**. The reaction is regioselective and the major products are **5a-d**. The minor products are varying amounts of **6a-d** and **7a,b**, depending upon the starting alkadiene used. The four major

Chart I



products were independently subjected to ozonolysis and yielded either *syn*- or *anti*-[1',8']naphthobicyclo[3.2.0]hept-2-ene-6-carboxaldehyde (Chart II). The stereo-

Chart II



chemistry of the anti aldehyde **8a** was determined by nmr analysis. The aldehydic proton of **8a** resonates at δ 9.97, whereas the aldehydic proton of *syn* aldehyde **8b** resonates at δ 9.33. This shielding difference is attributable to the positioning of the aldehydic proton of **8b** in the diamagnetic anisotropic shielding region of the naphthalene ring.^{5a} This effect is typically found in the cycloadducts of acenaphthylene.^{3,5b,c}

The coupling constant of the aldehydic proton of **8a** with its α hydrogen is 0.8 Hz, while *syn*-**8b** has a J value of 2.4 Hz between the aldehydic and α hydrogen. This suggests that different rotational constraints are imposed upon the carboxaldehyde function and that the effective coupling angle in the anti isomer is much smaller than in the *syn* isomer.⁶ We assume that the three hydrogens on the anti face of **8a** prohibit the rotation of the aldehyde group into a favored angle for maximum coupling.

The ozonolysis products from compounds **5a-d** were compared with the aldehydes **8a** and **8b** by standard glc techniques to ascertain the *syn* or *anti* relationship of the allyl substituent at the 6 position.

The *cis* or *trans* geometry of the allyl group was assigned on the basis of infrared and nmr data. Thus, both *cis* isomers **5b** and **5d** lacked the band at about 960 cm^{-1} that is characteristic of a *trans* disubstituted double bond.⁷ The *trans* isomers **5a** and **5c** both exhibited strong bands at about 960 cm^{-1} .

Decoupling of the methyl nmr doublet confirmed that it is coupled to the olefinic region in each isomer and allowed the coupling constants J_{FG} to be obtained for the isomers **5**. These experiments show that J_{FG} is 10.4 ± 0.3 Hz in isomers **5b** and **5d**. In isomer **5a** the value of J_{FG} is 14.8 ± 0.3 Hz. The nearly coincident chemical shifts of the olefinic hydrogens in isomer **5c** made the precision of measurement of J_{FG} difficult. However, a value of J of about 14 ± 1 Hz was measurable. The fact that J_{FG} is larger for isomers **5a** and **5c** than isomers **5b** and **5d** is further verification of the relative *cis* or *trans* geometry of the allyl group, because it is generally accepted that $J_{\text{trans}} > J_{\text{cis}}$ for olefinic isomers.⁸

Double irradiation of the vinyl region in the isomers **5** also decouples a signal assigned to proton H_C in the spectrum of each isomer (Table I). To protons H_A and H_B are assigned resonances in the δ 4 region. By elimination, H_D and H_E are assigned, the more shielded of the two is pre-

Table I. Nmr Chemical Shift Assignments for Isomers **5a-d** (δ)^a

Compd	H _A , H _B	H _C	H _D	H _E	H _F	H _G	CH ₃
5a	3.8-4.2	2.7	2.0-2.6	2.0-2.6	5.80	5.37	1.70
5b	3.8-4.3	3.1	2.4	2.4	5.77	5.42	1.55
5c	3.6-4.5	3.52	2.82	1.73	5.20	5.20	1.50
5d	3.6-4.5	3.82	2.93	1.7	4.90	5.18	1.65

^a Shifts relative to internal TMS in 5-10% solute concentrations in CCl₄.

sumed to be H_E . As the data indicate, the diamagnetic anisotropic shielding of the aromatic nucleus causes H_C to appear upfield, in **5a** and **5b** relative to the *syn* isomers **5c** and **5d**. Similarly, the olefinic hydrogens H_F and H_G are shifted upfield in *syn* isomers **5c** and **5d** relative to the olefinic protons in the *anti* isomers **5a** and **5b**. The methyl group chemical shift is variable. Apparently the distance between the methyl group and the aromatic nucleus is large enough to minimize anisotropic shielding effects that are found with other protons in the same molecule. Because of the complexity of the multispin set, we have reported only a few coupling constants for these molecules.⁹

The minor products have not been investigated in detail, although the data that we have obtained at this time are in complete agreement with the structures assigned in Chart I.

Photochemical Data. In Table II a comparison is made of the major product distribution that results in direct and sen-

Table II. Major Product Distribution from Direct and Sensitized Reaction of Acenaphthylene with *cis*- or *trans*-1,3-Pentadiene

Diene	Major product formed (%) ^a	
	Unsensitized	Sensitized
3	5b (49); 5d (42)	5b (50); 5d (43)
4	5a (50.5); 5c (41.0)	5a (51); 5c (42)

^a Percentage reported relative to total products detected.

sitized irradiations. The dicyclohexyl-18-crown-6-ether complex of the disodium salt of Rose Bengal was used in a manner identical with that in our previous study^{3a} to sensitize the triplet state reactions of **1** with **3** and **4** at a wavelength of 589 nm. The direct irradiations were carried out with light of wavelengths longer than 360 nm in the heavy-atom solvent dibromomethane. The product distributions are about the same.

Oxygen quenching of the reaction was verified by saturating photolysis mixtures with pure oxygen gas. Greater than 95% of the reaction was quenched when compared with quantum yields obtained in nitrogen degassed samples. This result is in contrast to observations made with cyclopentadiene.^{3a}

The reaction of **1** with *cis*-piperylene was studied as a function of the concentration of the diene in the solvents CH₂Br₂ and CH₃CN. It was found that the data conformed to a linear relation between the reciprocal of the quantum yield and the reciprocal of the diene concentration (Figures 1 and 2).

Discussion

Proposed Mechanism. The cogent evidence for the triplet nature of the reaction of acenaphthylene with cyclopentadiene is documented elsewhere.^{3a} The arguments cited there are equally applicable to the reactions of the piperylenes with **1**. The product ratios obtained in the direct and Rose Bengal sensitized irradiations between **1** and **3** or **4** are similar. Additionally, the unsensitized reactions between **1** and **3** or **4** are quenched by molecular oxygen. These data sup-

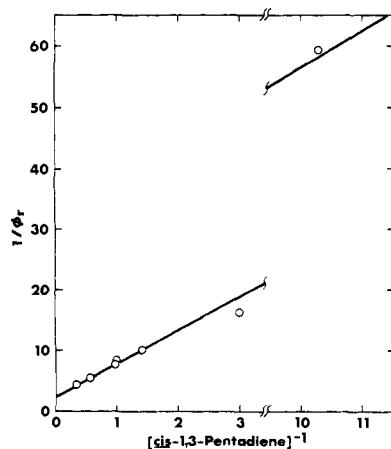
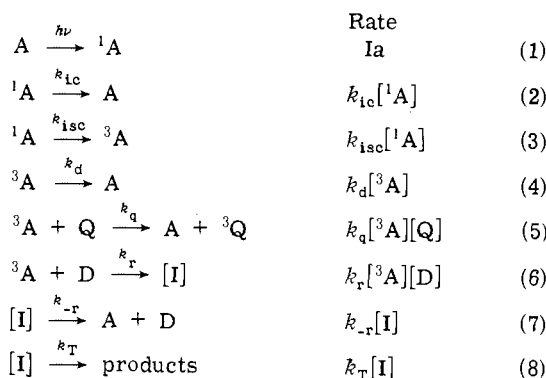


Figure 1. The dependence of ϕ_r upon different concentrations of *cis*-1,3-pentadiene reacting with 0.01 *M* acenaphthylene in dibromomethane.

port the intervention of excited triplet **1** in the mechanism of the reaction. The observations reported here conform to the previously proposed mechanism shown in Chart III.

Chart III



where A is acenaphthylene, D is diene, Q is quencher, I is intermediate, and k_{ic} , k_{isc} , k_d , k_q , k_r , k_{-r} , and k_T are respectively the rate constants for internal conversion, intersystem crossing ($S_1 \rightarrow T_1$), radiationless decay ($T_1 \rightarrow S_0$), quenching, intermediate formation, intermediate disproportionation, and the rate constant for product formation from I. We define α as the ratio $k_T/(k_{-r} + k_T)$, the fraction of intermediates that go on to product.

The steady-state kinetic treatment of the mechanism yields eq 9 for the quantum yield of product formation, ϕ_r . The reciprocal of this equation is expressed as eq 10 when $[Q] = 0$.

$$\phi_r = \alpha \left(\frac{k_{isc}}{k_{ic} + k_{isc}} \right) \left(\frac{k_r[D]}{k_r[D] + k_q[Q] + k_d} \right) \quad (9)$$

$$\frac{1}{\phi_r} = \frac{1}{\alpha\phi_{isc}} + \frac{k_d}{\alpha\phi_{isc}k_r} \left(\frac{1}{[D]} \right) \quad (10)$$

Concentration Study. Figures 1 and 2 show a least-squares plot of the data obtained from a study of the variation in quantum yield of product formed with a change in concentration of *cis* diene according to the mechanism implicit in eq 10.

In the solvent dibromomethane, a correlation coefficient of $r > 0.99$ corroborates the fit of the data, and the slope of the plot is $5.5 \pm 0.1 M^{-1}$ with an intercept of 2.2 ± 0.5 . From the reciprocal of the intercept, a value of $\alpha\phi_{isc}$ of 0.45 is obtained. The slope divided by the intercept produces a value for k_d/k_r of 2.5. This ratio is similar to the value of 2.2 obtained from a study of the reaction of **1** with cyclo-

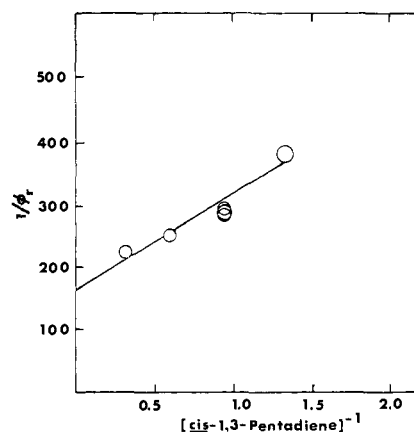


Figure 2. The dependence of ϕ_r upon different concentrations of *cis*-1,3-pentadiene reacting with 0.01 *M* acenaphthylene in acetonitrile.

pentadiene. This suggests that the values of k_d and k_r in the *cis*-piperylene reaction are about the same as those obtained in the cyclopentadiene study for the solvent CH_2Br_2 .

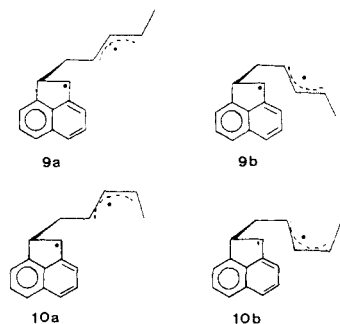
A comparison with the concentration dependence study in the solvent CH_3CN verifies the occurrence of the heavy-atom effect. The maximum quantum yield obtained for 3 *M* *cis* diene in acetonitrile was only 0.0043, a greater than 40-fold reduction in quantum yield from a similar reaction of **1** with *cis* diene in the solvent CH_2Br_2 . The acetonitrile data are subject to greater error because of the extremely small quantum yields. A least-squares treatment of the data obtained in the solvent CH_3CN yields a slope of $149 \pm 30 M^{-1}$ and an intercept of 167 ± 27 . A value of 0.006 for $\alpha\phi_{isc}$ is derived, and the ratio for k_d/k_r is computed to be 0.9. The correlation coefficient is 0.96.

Interpretation of $\alpha\phi_{isc}$. Assuming, as in our previous study,^{3a} that ϕ_{isc} is 1 in heavy-atom solvents, we obtain a value of 0.45 for α in the *cis*-piperylene reaction with **1**. This value is approximately twice the value of 0.2 for α in the cyclopentadiene reaction and suggests that the intermediate derived from **3** more efficiently forms product than the intermediate derived from cyclopentadiene. For acetonitrile, a value of $\phi_{isc} \leq 0.013$ is computed on the assumption that α remains equal to 0.45. This value compares favorably, within the experimental uncertainties, with the value for ϕ_{isc} obtained for **1** reacting with cyclopentadiene in acetonitrile.^{3a} This again emphasizes the extreme inefficiency of intersystem crossing in acenaphthylene in the absence of heavy atom perturbation. The k_d/k_r ratio for **1** reacting with **3** in CH_3CN is of similar magnitude to the cyclopentadiene study, and the calculated standard deviations suggest that based on minor differences any interpretation would be equivocal.

Postulated Intermediate. The postulated intermediate in these reactions could be a triplet diradical or a triplet exciplex. A triplet exciplex was proposed to explain the inefficient sensitized dimerization of indene.¹⁰ However, we have suggested that a triplet biradical is the probable intermediate that occurs when cyclopentadiene reacts with excited triplet **1**.^{3a}

In the piperylene reaction for triplet **1** reacting with either *cis*- or *trans*-piperylene, a 90% regioselectivity is found for the terminal double bond. This is typical since terminal double bonds are generally more susceptible to attack than internal double bonds.¹¹ The reactions to form the major products are also stereoselective in that the *cis* or *trans* geometry of the starting diene is maintained in the major products formed from each reactant. The maintenance of the stereochemical integrity of the starting diene in the major products is consistent with the formation of a

diradical intermediate that has allylic stabilization. Thus, diradicals **9a,b** are expected to form products derived only from *trans*-piperylene, whereas diradicals **10a,b** are expected to form products derived only from *cis*-piperylene. Our data are thus in accord with literature expectations that suggest that at modest temperatures allylic units are expected to maintain their stereochemical integrity.¹²



Because explicit knowledge of the behavior of triplet exciplexes is not available, we can only mount circumstantial evidence against their presence in our system. If triplet exciplexes are capable of causing isomerization of *cis*-piperylene, then we anticipate that some isomerization of *cis*-piperylene would be detected in the reaction of **1** with **3**. However, in the direct irradiation studies no detectable increase in *trans* diene was found. Thus, the intermediate that reduces the efficiency of the reaction does not concurrently cause observable isomerization of *cis*-piperylene.¹³

The amount of isomerization of **3** occurring was investigated during the sensitized reactions of **1** with **3** using the crown ether complex of Rose Bengal. A small but experimentally verifiable amount of isomerization of **3** to **4** was detected. A separate sample of *cis*-piperylene and the Rose Bengal complex was irradiated in CH_2Br_2 and in CH_3CN . In both tubes, detectable isomerization of **3** to **4** occurred in the absence of acenaphthylene. Thus, the dye Rose Bengal ($E_T = 44.6$ kcal)^{3a} is slowly sensitizing the isomerization of *cis*-piperylene ($E_T = 57.3$ kcal)¹⁴ by an apparently endothermic process. In the absence of **1**, the sensitized *trans*-piperylene runs indicated only trace amounts of isomerization to *cis*-piperylene.

The similarities in the triplet energies of **1** and Rose Bengal^{3a} lead us to believe that **1** should cause *cis*-piperylene to isomerize if a triplet exciplex between **1** and **3** occurs. The absence of significant isomerization of **3** to **4** in the direct irradiation studies with **1** present further suggests that the intervention of a triplet diradical intermediate is the energy-wasting step in this system.

The relative proportions of *syn* and *anti* isomers in each group of major products are consistent with a diradical intermediate. Both *cis*- and *trans*-piperylene give slightly more *anti* product than *syn* product. If secondary forces, such as maximum accumulation of orbitals in an exciplex, contribute to its stability, then a near 50:50 product distribution of both *syn* and *anti* products does not seem consistent with an exciplex mechanism.^{10b}

A comparison of the differing efficiencies of reaction between **1** and cyclopentadiene and **1** and the piperylenes leads to the conclusion that diradicals are involved as intermediates, but that the activation energy for ring closure is lower for diradicals **9** and **10**. A rationalization for this higher efficiency is found in the nature of the products being formed. We assume that the activation energy for ring closure of the diradical is higher in the cyclopentadiene reactions because tricyclic structures are being formed that have more strain energy than the bicyclic products derived from the piperylenes.

The fact that cyclopentadiene is structurally more rigid than the piperylenes might also be an additional factor. The diradicals **9** and **10** might be able to achieve conformations that more readily close to a ring than the conformations available to a diradical composed of **1** and **2**.

Minor Products. The minor products contribute less than 10% to the overall product mixture obtained from **3** or **4**. The small yields of minor products were not conducive to an extensive structural analysis. However, we have verified that some [2 + 2] cycloaddition between **1** and **3** or **4** occurs with the internal double bond of the diene. The products thus formed are isomers of 6-methyl-7-vinyl-[1',8']naphthobicyclo[3.2.0]hept-2-ene (**6**). We ascribe the small yield of isomeric **6** to the lesser reactivity of the internal double bond. This is probably a reflection of both electronic effects and steric effects in the transition state that leads to these products.

A small yield (< 3.0%) of the [4 + 2] cycloadduct **7** was verified in the reaction between **1** and *trans*-diene **4**, but no detectable **7** was found in the reaction between **1** and **3**. This selectivity for a [4 + 2] cycloaddition between a dienophile and isomers **3** and **4** is well known¹⁵ for ground-state reactions. It is noteworthy that it occurs in a triplet excited-state reaction as well.

The stereochemistry of the isolated photoproduct mixture **7a,b** was compared with that obtained by reacting **1** with **4** in a sealed tube at 160°. The nmr spectrum of photomixture **7a,b** showed the same resonances as the thermal Diels-Alder product, but the proportion of the two expected [4 + 2] isomers differed. The stereochemistry of the thermal product has never been proved.¹⁶ If, as is typical in many [4 + 2] reactions between simple hydrocarbons, the *syn* isomer predominates,¹⁵ we then find that by comparison the *anti* stereochemistry predominates in the photoproduct mixture. This is analogous to the result found in the [4 + 2] reaction between **1** and cyclopentadiene.^{3a}

There is general agreement that the thermal [4 + 2] reaction is concerted.¹⁵ Whether or not the photochemical [4 + 2] component of this reaction is stepwise or concerted remains to be proved.

Conclusion

The evidence from the data reported here is circumstantial but in agreement with the supposition that the products derived from excited triplet **1** reacting with **3** or **4** are produced from an intermediate that is a triplet diradical. Thus, several steps are required before product is formed. The triplet diradical must undergo intersystem crossing to a singlet diradical which can then collapse to product or dissociate to starting materials. The efficiency with which the diradical goes to form product is apparently a function of the activation energy required to close the ring. Conformational rigidity in the starting diene and ring strain in the polycyclic products produced appear to be factors influencing the overall efficiency of the reaction as the transition state is reached.²²

Experimental Section

Materials. Acenaphthylene was purified as previously described.^{3a} *Cis*-1,3-Pentadiene was prepared by treating maleic anhydride with a mixture of piperylene isomers (Aldrich) and distilling the *cis*-piperylene.¹⁷ It contained less than 0.05% of the *trans* isomer by glc measurement. Pure *trans*-1,3-pentadiene (99.9+%) was purchased from Chem Samp Co., Columbus, Ohio. Benzophenone (Eastman, White Label) was purified by repeated crystallization from ethanol. The crown ether complex of Rose Bengal was available from a previous study.^{3a} Solvents were routinely dried over Linde 5A molecular sieves and freshly distilled through a 1-m Vigreux fractionating column.

Instrumentation. Glc analyses were performed with a Varian 1200 Hi-Fi connected to a Sargent SR recorder equipped with Disc integrator. Column A was a 7 ft \times 0.125 in. 3% OV-17 on 80–100 mesh Chromosorb W. Column B was a 4 ft \times 0.25 in. stainless steel column with 33% AgNO₃-ethylene glycol on 80–100 mesh Chromosorb W. Preparative scale glc separations were performed on a Varian 920 using a 2 ft \times 0.25 in. column of 10% OV-17 on 80–100 mesh Chromosorb W (column C). Infrared spectra of thin films of liquid samples or of KBr pellets of solid samples were obtained on a Perkin-Elmer 337 spectrometer. Ultraviolet measurements were obtained from a Beckmann DU-2 or DB-G recording spectrophotometer. A Varian T-60 nmr spectrometer equipped with frequency decoupler was used to obtain nmr spectra from dilute solutions of solute dissolved in CDCl₃ or CCl₄ at 34°. A Finnegan 1015C System/150 computer controlled ensemble with gas chromatograph was used to generate mass spectra at 70 eV ionizing radiation. Melting points were obtained from a Fisher-Johns apparatus and are uncorrected. Elemental analyses were obtained from Galbraith Laboratories, Knoxville, Tenn.

Irradiation Procedures. Direct irradiations of solutions of **1** were performed with a 450-W Hanovia lamp housed in a Pyrex immersion well with circulating cold copper nitrate solution (0.7 M) and surrounded by filters of Corning Glass CS-7-60 so that only a narrow band of light between 360 and 390 nm was transmitted.¹⁸ This combination was placed in the center of Rayonet MGR-500 merry-go-round apparatus contained in a specially designed box sealed to keep out stray light. The actinometer solutions were irradiated in parallel with the reaction mixtures. All runs were carried to low conversions of reactant (<20%), and concentrations were adjusted so that the molar absorbance of **1** was always greater than 3.0 after cessation of the reaction. Degassing procedures and sensitized irradiations were performed as previously described.^{3a}

Analyses. Photolysis mixtures containing products derived from **1** were analyzed on column A at 155°. Internal standards were acenaphthene and 5-acenaphthaldehyde for unreacted **1** and photoproducts **5**, **6**, and **7**, respectively. The analytical procedure used is identical with that described in a previous study.^{3a}

Actinometry. The benzophenone-sensitized isomerization of *trans*-stilbene was used as the actinometer¹⁹ with correction for back isomerization.²⁰

Benzil was also used as a sensitizer in the *trans*-stilbene mixtures to corroborate the fact that benzophenone was absorbing all the available light that would be absorbed by acenaphthylene.^{3a}

The cycloadducts and solvents were shown to have insignificant absorption at the wavelength used for quantum yield determinations.

anti-(8a) and syn-[1',8']Naphthobicyclo[3.2.0]hept-2-ene-6-carboxaldehyde (8b). To a magnetically stirred mixture of 100 ml (1.0 mol) of isomeric 1,3-pentadienes (70% *trans*, 30% *cis*) and 230 ml of dibromomethane contained in an Hanovia immersion apparatus with circulating cold copper nitrate solution (0.7 M) and continuously purged with nitrogen was added 10.0 g (0.66 mol) of acenaphthylene in 1-g portions while irradiating for 1 hr. When the solution was almost colorless, irradiation was stopped, and rotary evaporation (water aspirator) of the reaction mixture yielded 19 g of a pale yellow oil. Suction filtration of this oil removed about 0.3 g of the *trans* photodimer of **1**. Glc of the oil on a 4 ft \times 0.25 in. 3% OV-1 column at 160° recorded peaks with the following relative retention times (% total area): 1.00 (2), 1.07 (2), 1.32 (32), 1.65 (63), 2.04 (1).

In 40 ml of glacial acetic acid was dissolved 1.0 g of the crude photoproduct mixture. The mixture was treated with ozone, reduced with zinc, and worked up according to the procedure of Nolter and Adams²¹ to yield 640 mg of yellow oil that by glc at 180° on 3% OV-1 is two components in a 2:1 area ratio with relative retention times of 1.00 and 1.10. The oil was chromatographed on 20 g of silica beginning with ligroin as the eluent and ending with a 20% benzene-ligroin mixture. Early fractions were rich in anti isomer and later fractions were rich in syn isomer.

The anti isomer **8a** was crystallized from hexane and then sublimed (50° (0.025 mm)) to yield colorless crystals, mp 53–55°; nmr (CCl₄) δ 1.8–2.3 (m, 1 H), 2.7–3.2 (m, 2 H), 3.9–4.5 (m, 2 H, ArCH₂), 7.1–7.7 (m, 6 H, ArH), 9.97 ppm (d, 1 H, CHO, J = 0.8 Hz); ir (KBr) 3020, 2930, 2780, 2690 (C–H), 1710 (C=O), 1600 (C=C), 1490, 1360, 821, 780 cm⁻¹. Anal. Calcd for C₁₅H₁₂O: C, 86.51; H, 5.81. Found: C, 86.37; H, 5.81.

The oily syn isomer **8b** was recrystallized from hexane to yield colorless crystals, mp 81–83°; nmr (CCl₄) δ 2.0–3.0 (m, 2 H), 3.58 (q, 1 H, J = 8 Hz), 4.0–4.8 (m, 2 H, ArCH₂), 7.1–7.7 (m, 6 H, ArH), 9.33 ppm (d, 1 H, CHO, J = 2.4 Hz); ir (KBr) 3020, 2930, 2800, 2710 (C–H), 1710 (C=O), 1610, 1600 (C=C), 1490, 1430, 1360, 1182, 1099, 821, 781 cm⁻¹. Anal. Calcd for C₁₅H₁₂O: C, 86.51; H, 5.81. Found: C, 86.50; H, 5.82.

anti-6-(trans-1-Propenyl)[1',8']naphthobicyclo[3.2.0]hept-2-ene (5a) and Syn-Trans Isomer 5c. A Rayonet RPV-8 Pyrex test tube was charged with 4.5 ml of *trans*-1,3-pentadiene and sufficient dibromomethane added to adjust the volume to 15 ml. Acenaphthylene, 22.5 mg (0.15 mmol), was added, and the solution was degassed with nitrogen for 25 min. The solution was then irradiated until the yellow of **1** was discharged (about 12 min). Additional portions of about 22 mg of **1** were added to the mixture, and irradiation was continued until a total of 496 mg (3.2 mmol) of **1** was consumed over a period of about 4 hr. Rotary evaporation of the photolysate (water evaporator) afforded 790 mg of a tan oil. Analytical glc analysis of this oil on column A at 180° gave the following relative retention times (% total area): 1.00 (2.4), 1.08 (1.8), 1.27 (2.6), 1.48 (41), 1.77 (50), 2.30 (2).

Preparative glc of this oil on column C at 155° effected separation of three peaks with relative retention (R_1) of 1.00, 1.48, and 1.77. Peak R_1 = 1.0 (assumed to be an isomer of **6**) was a colorless solid that after crystallization from hexane and sublimation (40°, 0.025 Torr) had mp 47.5–48.5°; nmr (CCl₄) δ 1.32 (d, 3 H, methyl, J = 6.4 Hz), 2.02 (q, 1 H, CH₃CH, J = 7 Hz), 3.00 (q, 1 H, allylic methine, J = 8 Hz), 3.62 (t, 1 H, benzylic, J = 6 Hz), 4.30 (AB q, 1 H, benzylic, J = 6, 10 Hz), 4.73 (d, 1 H, vinylic, J = 2.8 Hz), 4.95 (AB q, 1 H, vinylic, J = 2.8, 7.6 Hz), 5.52 (q, 1 H, vinylic, J = 8 Hz), 7.1–7.7 ppm (m, 6 H, aromatic); ir (KBr) 3030, 2940 (C–H), 1610 (C=C), 1450, 1360, 908, 781 cm⁻¹; mass spectrum (70 eV) m/e (rel intensity) 220 (3), 153 (13), 152 (100), 151 (9), 39 (8). Anal. Calcd for C₁₇H₁₆: C, 92.68; H, 7.32. Found: C, 92.73; H, 7.33.

Peak R_1 = 1.48, isomer **5c**, was isolated as a colorless oil which slowly crystallized on standing, mp 36–38°; nmr (CCl₄) δ 1.50 (d, 3 H, methyl, J = 4.4 Hz), 1.73 (m, 1 H), 2.82 (q, 1 H, J = ~10 Hz), 3.52 (p, 1 H, allylic methine, J = ~8 Hz), 3.8–4.5 (m, 2 H, benzylic), 4.8–5.6 (m, 2 H, vinylic), 7.0–7.6 ppm (m, 6 H, aromatic); ir (neat) 3020, 2920, 2840 (C–H), 1600 (C=C), 1480, 1440, 1430, 1360, 967 (trans RC=CR), 820, 779 cm⁻¹; mass spectrum (70 eV) m/e (rel intensity) 220 (6), 165 (15), 153 (13), 152 (100), 151 (21). Anal. Calcd for C₁₇H₁₆: C, 92.68; H, 7.32. Found: C, 92.55; H, 7.29.

Peak R_1 = 1.77, isomer **5a**, was collected as a pale yellow oil: nmr (CCl₄) δ 1.70 (d, 3 H, methyl, J = 5.4 Hz), 2.0–2.9 (m, 3 H), 3.8–4.2 (m, 2 H, benzylic), 5.1–6.0 (m, 2 H, vinylic), 7.1–7.6 ppm (m, 6 H aromatic); ir (neat) 3020, 2920, 2840 (C–H), 1600 (C=C), 1490, 1430, 1360, 966 (trans RC=CR), 822, 780 cm⁻¹; mass spectrum (70 eV) m/e (rel intensity) 220 (12), 165 (12), 153 (59), 152 (100), 151 (29), 150 (13), 52 (9), 41 (13), 39 (21). Anal. Calcd for C₁₇H₁₆: C, 92.68; H, 7.32. Found: C, 92.50; H, 7.30.

7-Methyl-6b,7,10a-tetrahydrofluoranthene (7a and 7b). A 2 \times 40 cm column of 5% silver nitrate on silica gel (Curtin, 60–200 mesh) was charged with 500 mg of crude photolysate from the *trans*-piperylene run, and the column was eluted with 275 ml of 1:9 (v/v) benzene-hexane followed by 275 ml of 2:8 (v/v) benzene-hexane to remove isomers **5** and **6**. Subsequent elution with 200 ml of 1:1 (v/v) benzene-hexane afforded 17 mg of a pale yellow oil. Preparative glc of this oil on column C at 160° separated pure **7** as a colorless solid that after sublimation (40°, 0.025 Torr) had mp 66.5–67.5°; nmr (CCl₄) δ 1.48 (d, 3 H, methyl, J = 6.8 Hz), 1.9–2.4 (m, 2 H), 2.80 (m, 1 H), 3.33 (t, 1 H, benzylic, J = 8 Hz), 3.78 (q, 1 H, benzylic, J = 8 Hz), 5.83 (broad s, 2 H, vinylic), 7.1–7.7 ppm (m, 6 H, aromatic); ir (KBr) 3020, 2920 (C–H), 1610 (C=C), 1380, 820, 779, 724, 673 cm⁻¹; mass spectrum (70 eV) m/e (rel intensity) 220 (10), 153 (14), 152 (100). Anal. Calcd for C₁₇H₁₆: C, 92.68; H, 7.32. Found: C, 92.84; H, 7.17. Examination of the nmr spectrum of the **7a,b** mixture isolated as described above provides an estimate of 30% **7b** and 70% **7a** by relative integration of the methyl doublet region.

Thermal Formation of Presumed 7b. A 1 \times 20 cm Carius tube was charged with 1.0 g of **1** (about 6 mmol), 2.0 ml (20 mmol) of **4**, and 10 mg of hydroquinone in 1 ml of THF. The tube was sealed, heated to 160° for 12 hr, and opened at 0°; the solvent was

removed by rotary evaporation to produce 2.1 g of a red oil. Chromatography of this oil on a column composed of 5% silver nitrate on silica gel followed by preparative glc on column C at 160° followed by recrystallization from hexane yielded colorless needles, mp 88.5–90.0° (lit.¹⁶ 94–95°); nmr (CCl₄) δ 1.23 (d, 3 H, methyl, *J* = 7.2 Hz), 1.47 (d, 0.20 H, methyl doublet of side product, presumed **7a**), 2.5–2.8 (m, 3 H), 3.8–4.0 (m, 2 H, benzylic), 5.62 (d, 2 H, vinylic), 7.1–7.6 ppm (m, 6 H, aromatic); ir (KBr) 3030, 2960, 2840 (C–H), 1610 (C=C), 1380, 820, 779, 718, 659 cm⁻¹; mass spectrum (70 eV) *m/e* (rel intensity) 220 (7), 219 (2), 152 (100), 151 (42). *Anal.* Calcd for C₁₇H₁₆: C, 92.68; H, 7.32. Found: C, 92.71; H, 7.34.

anti-6-(cis-1-Propenyl)[1',8']naphthobicyclo[3.2.0]hept-2-ene (5b) and Syn-Cis Isomer 5d. The procedure described for the reaction of *trans*-1,3-pentadiene was used to treat 495 mg (3.2 mmol) of **1** with 4.5 ml of **3** during an irradiation interval of 276 min. Removal of solvent by rotary evaporation (water aspirator) gave 1.08 g of a tan oil. Analysis of this oil on column A at 160° gave the following relative retention times (% total area): 1.00 (1.1), 1.08 (3.9), 1.28 (2), 1.36 (2), 1.76 (50), 1.91 (43).

A 2 × 40 cm column of 5% silver nitrate on silica gel was charged with the oil and eluted with 250 ml of 1:9 (v/v) benzene-hexane (fraction I). The eluent was changed to a 2:8 (v/v) benzene-hexane mixture, and 100 ml was collected. The next 200 ml was collected and combined with a subsequent 100-ml volume obtained by eluting the column with 1:1 (v/v) benzene-hexane (fraction II). Rotary evaporation of fraction I yielded 252 mg of a colorless oil. Preparative glc of this oil on column C at 160° achieved separation of a minor component, *R*_t = 1.08, as a colorless oil that slowly crystallized on standing, mp 51.5–53.0°; ir (neat) 3040, 2985, 2960, 2940, 2860, 992, 913, 826, 795, 774 cm⁻¹; mass spectrum (70 eV) *m/e* (rel intensity) 220 (9), 165 (8), 153 (8), 152 (100), 151 (18), 39 (12). The small sample yield precluded any further identification of the structure.

The major component isolated from fraction I by glc, *R*_t = 1.76, isomer **5b**, was obtained as a pale yellow oil: nmr (CCl₄) δ 1.55 (d, 3 H, methyl, *J* = 6.2 Hz), 2.0–2.8 (m, 2 H), 3.1 (m, 1 H, allylic methine), 3.8–4.3 (m, 2 H, benzylic), 5.2–6.0 (m, 2 H, vinylic), 7.1–7.7 ppm (m, 6 H, aromatic); ir (neat) 3030, 3000, 2920, 2840 (C–H), 1600 (C=C), 1490, 1440, 1360, 822, 780 cm⁻¹; mass spectrum (70 eV) *m/e* (rel intensity) 220 (1), 154 (10), 152 (100). *Anal.* Calcd for C₁₇H₁₆: C, 92.68; H, 7.32. Found: C, 92.58; H, 7.27.

Rotary evaporation of fraction II gave 161 mg of a yellow solid that was dissolved in warm hexane. Colorless prisms of component *R*_t = 1.91, isomer **5d**, separated upon refrigeration. These were recrystallized from hexane to yield 20 mg of **5d**, mp 87.0–89.0°; nmr (CCl₄) δ 1.65 (d plus underlying peaks, 4 H, methyl, *J* = 5.0 Hz, plus one proton from cyclobutane ring), 2.93 (q of unequal couplings, 1 H), 3.6–4.5 (m, 3 H, benzylic and allylic methines), 5.18 (m, 2 H, vinylic), and 7.1–7.7 ppm (m, 6 H, aromatic); ir (KBr) 3010, 2950, 2910, 2830 (C–H), 1590 (C=C), 1480, 1430, 1360, 821, 781 cm⁻¹; mass spectrum (70 eV) *m/e* (rel intensity) 220 (2), 165 (8), 153 (11), 152 (100), 151 (10), 39 (10). *Anal.* Calcd for C₁₇H₁₆: C, 92.68; H, 7.32. Found: C, 92.46; H, 7.25.

The mother liquor from the recrystallization of compounds isolated in fraction II was subjected to preparative glc on column C at 160° to give component *R*_t = 1.00 (presumed isomer **6**) as a colorless oil that crystallized on standing, mp 49.5–51.0°; ir (neat) 3050, 2975, 2950, 2920, 2890, 2865, 1605, 1450, 1365, 990, 900, 824, 774 cm⁻¹; mass spectrum (70 eV) *m/e* (rel intensity) 220 (3), 152 (100), 151 (12), 150 (8), 39 (12). The small isolated yield precluded further structure determination.

Rose Bengal Sensitized Irradiations of the Isomeric 1,3-Pentadienes. In a typical run a 12 × 75 mm Pyrex test tube was charged with 0.65 ml (6.6 mmol) of diene and 1.50 ml of 0.455 *M* disodium bis(cyclohexyl-18-crown-6 ether)-Bengal Red complex^{3a} in dibromomethane. The tube was sealed with a rubber septum, and the solution was degassed with nitrogen for 10 min. The solution was irradiated with a sodium vapor lamp for 160 min and then analyzed on column B in series with column A at 30°. The results obtained are shown in Table III.

Ozonolysis of Components Isolated by Chromatography of the Photoproduct Mixture. Each component isolated from the crude

Table III

Compd	Solvent	% isomer before irradiation	% isomer after irradiation
3	CH ₂ Br ₂	0.05 (trans)	0.64 (trans)
3	CH ₃ CN	0.05 (trans)	0.72 (trans)
4	CH ₃ CN	0.00 (cis)	0.21 (cis)

photoproduct mixture was dissolved in 4.0 ml of ethyl acetate (purified by passage over alumina) in a 10-ml round-bottom flask cooled in ice-water, and a slow stream of ozone mixed with air was bubbled through the solution for 80 sec. Subsequently, 9.5 mg of platinum oxide was added, and the flask was flushed with hydrogen and magnetically stirred under 1 atm of hydrogen for 30 min. After evaporation of solvent, the residual aldehyde was analyzed by ir, nmr, and glc to confirm its structure and thereby confirming the syn or anti stereochemistry of the original allylic moiety.

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