Mechanisms of Photochemical Reactions in Solutio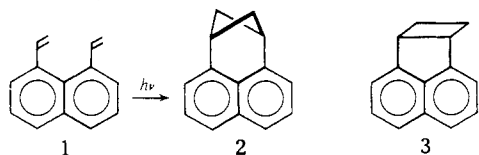n. LXXXI.[1] Photocyclization of 1,8-Divinylnaphthalene. A New Method for Determining the Multiplicity of Excited State Intermediates

Ronald H. Fleming, Frank H. Quina, and George S. Hammond*

Contribution from the Division of Natural Sciences, University of California at Santa Cruz, Santa Cruz, California 95064. Received March 19, 1974

Abstract: 1,8-Divinylnaphthalene has been irradiated in the presence of varying amounts of bromocyclopropane. The quantum yield for product formation was enhanced even though 1,8-divinylnaphthalene fluorescence was quenched. This behavior indicates that the product was formed from the *triplet* excited state of 1,8-divinylnaphthalene. Quantitative treatment of the enhancement and quenching data showed that the intersystem crossing quantum yield (Φ_{isc}) was 0.25. The quantum yields for fluorescence (Φ_f) and for product formation (Φ_p) were measured by standard procedures (0.71 and 0.16, respectively), and the quantum yields for radiationless decay of the S_1 and T_1 states were estimated. The measured fluorescence lifetime (1.4 nsec) inicated the absolute rate of processes leading from S_1.
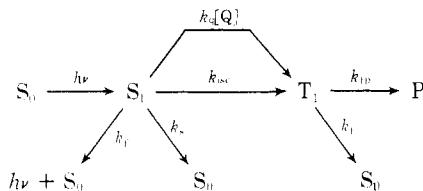
The photodimerization of two aryl-substituted ethylene moieties gives cyclobutane rings. This familiar reaction was first illustrated by Ciamician and Silber[2] and Stobbe[3] in their photochemical studies of stilbene and styrene derivatives. More recently, ultraviolet irradiation of 1,8-divinylnaphthalene (1) by Meinwald and coworkers[4] led to production of *peri*-naphthobicyclo[3.1.1]heptene (2) and *peri*-naphthobicyclo[3.2.0]heptene (3) in a 10:1 ratio. We undertook the present studies on this system partly in order to elucidate the interrelationships between the photophysical and photochemical processes involved. In addition, we hoped to develop a new type of mechanistic probe utilizing heavy-atom enhancement of intersystem crossing as suggested by Carroll and Quina.[5]

Results and Discussion

Our procedure requires two conditions. First, the starting material (1) must fluoresce (*vide infra*), and, second, a quencher (Q) must be available which quenches the excited singlets by causing them to cross to triplets. This latter condition is fulfilled by heavy-atom quenchers.[5] If product formation occurs directly from the same intermediate (S_1) as fluorescence, then both processes must be quenched at the same rate. If, on the other hand, the reaction pathway includes the excited triplet manifold, then higher concentrations of quencher would cause faster intersystem crossing, higher triplet yields, and ultimately a greater quantum yield of products (see Scheme I). A quantitative expression has been derived[5,6] which relates the unimolecular intersystem crossing quantum yield (Φ_{isc}) to relative quantum yields of fluorescence and product formation, with and without quencher. The ratio, eq 1, of product quantum yields in the

Scheme I

$$\frac{\Phi_p}{{}^0\Phi_p} = \frac{\left(\frac{k_{isc} - k_q[Q]}{k_f + k_s + k_{isc} + k_q[Q]}\right)\left(\frac{k_{tp}}{k_{tp} + k_t}\right)}{\left(\frac{k_{isc}}{k_f + k_s + k_{isc}}\right)\left(\frac{k_{tp}}{k_{tp} + k_t}\right)} \tag{1}$$

$$\frac{{}^0\Phi_f}{\Phi_f} = 1 + k_q\tau[Q] \tag{2}$$

$$\tau = \text{fluorescence lifetime} = \frac{1}{k_f + k_s + k_{isc}}$$

$$\frac{{}^0\Phi_f}{\Phi_f} - 1 = \Phi_{isc}\left(\frac{{}^0\Phi_f}{\Phi_f}\frac{\Phi_p}{{}^0\Phi_p} - 1\right) \tag{3}$$

presence and absence of quencher was combined with eq 2, the standard Stern–Volmer quenching relationship, to give eq 3. In eq 1, k_{isc}, k_f, and k_s are the unimolecular rate constants of intersystem crossing, fluorescence, and internal conversion of S_1 to S_0, respectively, and k_q is the bimolecular quenching rate constant. Conversions of T_1 giving product and starting material have unimolecular rate constants k_{tp} and k_t, respectively. Since no detectable amounts of products other than 2 and 3 were found (*vide infra*), we assumed that $-\Phi_1 = \Phi_2 + \Phi_3 = \Phi_p$ and monitored the reaction by spectrophotometric determination of the disappearance of 1. It can be seen from eq 3 that only *relative* quantum yields of fluorescence and chemical reaction need to be measured. Furthermore, it is not necessary to know the quencher concentration.

There are some problems, however, in the selection of an appropriate quencher. Xenon has several desirable properties: it is inert and it has favorable spin–orbit coupling parameters. However, it is not very soluble in organic solvents, it is somewhat inconvenient to work with, and it is expensive. Iodo compounds all absorb too much light at the irradiation wavelength (313 nm). Aromatic bromo derivatives also absorb substantially. For example, the absorbance of neat bromobenzene at 313 nm is about 0.75 with benzene as reference. *n*-Bromobutane was tried, and it quenched fluorescence as expected. However, on longer irradiation, somewhat erratic product quantum yields were observed. This behavior was tentatively attributed to the intervention of radical chain processes involving bromine atoms and butyl radicals which might have consumed 1 at varying unpredictable rates. Bromocyclopropane was chosen as quencher with the expectation that side reactions of this type would be minimized since cyclopropyl radicals are formed only with relative difficulty.[7] Neat bromocyclopropane had ab-
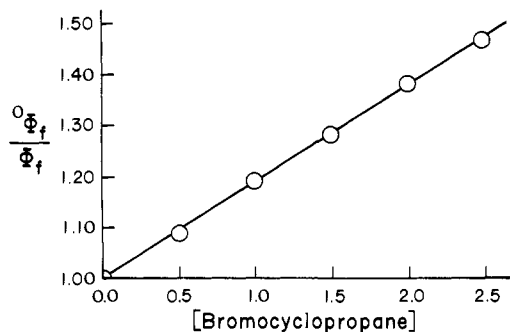
Figure 1. Stern–Volmer treatment of fluorescence quenching of 1 by bromocyclopropane.

Figure 2. Determination of the intersystem crossing quantum yield of 1.

sorbances (1-cm path) of 0.062 and 0.123 at 345 and 313 nm, respectively (with benzene as reference).

Several benzene solutions were prepared in which the concentration of 1 remained constant at 5.2×10^{-4} M, and the concentration of bromocyclopropane was varied from 0.0 to 2.5 M. The absorbance of 1 at 313 nm was calculated as 5.33, and it was measured at 345 nm as 0.953. Thus bromocyclopropane absorbed 0.46% of the light at 313 nm and 1.3% at 345 nm for the most concentrated sample.

The relative fluorescence (λ_{max} 385 nm) of the various solutions was determined with 345-nm excitation. These data (Table I) were treated by the normal Stern–Volmer procedure (eq 2) and are illustrated in Figure 1. The least-squares value for $k_q\tau$ was 0.190 with a correlation coefficient of 0.9996. The fluorescence lifetime of 1 was 1.4 nsec $\pm$ 20%, and k_q was about 1.4×10^8 l. mol^{-1} sec^{-1}.

The above samples were irradiated at 313 nm in a merry-go-round apparatus.[8] The amount of 1 remaining was determined by ultraviolet spectrophotometry at 345 nm, and two corrections were made to the data. The first correction was for the amount of light absorbed (up to 1.3%) by bromocyclopropane during analysis for 1, and the second was for the amount of light absorbed by bromocyclopropane during the irradiation. The corrected data are shown in Table I and plotted in Figure 2. The intersystem crossing quantum yield was determined from the least-squares slope: $\Phi_{isc} = 0.25$ (correlation coefficient 0.9994).

In the presence of quencher, the rate of disappearance of 1 was enhanced, and the relative quantum yields followed eq 3 indicating that most, or all, of the reaction arises from the triplet manifold. The mechanism of Scheme I is the simplest formulation, although involvement of high triplets cannot be excluded.

Although Scheme I and eq 3 are adequate to describe the experimental results, it is interesting to consider explicitly the possibility that the heavy-atom quencher facilitates intersystem crossing of excited triplet 1,8-divinylnaphthalene molecules to their ground state, i.e., eq 4, where k_{tq} is the

$$ T_1 \xrightarrow{k_{tq}[Q]} S_0 \qquad (4) $$

bimolecular rate constant for the process. Equation 1 can then be modified to eq 5 which upon combination with the

Table I. Relative Quantum Yield Data
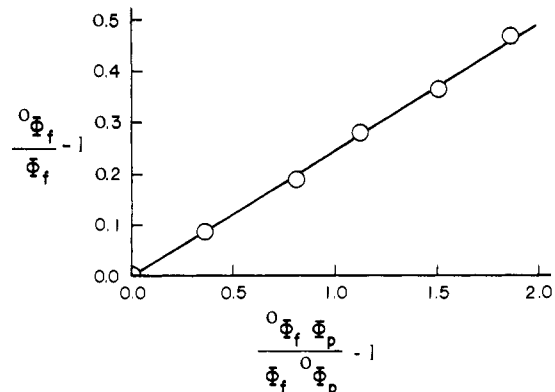
[Bromocyclopropane]	$^0\Phi_f/\Phi_f$ (rel)	$\Phi_p/^0\Phi_p$
0.00	1.000	1.000
0.50	1.08 (7)	1.25 (2)
0.99	1.18 (9)	1.52 (3)
1.49	1.28 (1)	1.65 (4)
1.99	1.38 (4)	1.81 (6)
2.48	1.46 (5)	1.95 (1)

Stern–Volmer expression and the rearrangement of terms gives eq 6 where τ_t is the unperturbed triplet lifetime.

$$ \frac{\Phi_p}{^0\Phi_p} = \frac{\left(\dfrac{k_{isc} + k_q[Q]}{k_s + k_f + k_{isc} + k_q[Q]}\right)\left(\dfrac{k_{tp}}{k_p + k_{tp} + k_{tq}[Q]}\right)}{\left(\dfrac{k_{isc}}{k_s + k_f + k_{isc}}\right)\left(\dfrac{k_{tp}}{k_p + k_{tp}}\right)} \qquad (5) $$

$$ \frac{\Phi_{isc} + (^0\Phi_f/\Phi_f) - 1}{\Phi_{isc}(\Phi_p{}^0\Phi_f/^0\Phi_p\Phi_f)} = 1 + k_{tq}\tau_t[Q] \qquad (6) $$

Analysis of the data of Table I according to eq 6 shows that $k_{tq}\tau_t$ is not significant, and that there is no detectable heavy atom quenching of triplet 1.

We suspected that the minor product 3 might arise from S_1. In order to test this possibility, larger samples of 1 were irradiated in degassed benzene solutions with and without added bromocyclopropane. In both cases, the reaction went to completion without the formation of any other products. In the absence of bromocyclopropane, the ratio of 3 to 2 (by nmr) was 1:22, in fair agreement with Meinwald and co-workers.[4] No 3 at all was detected in the presence of quencher. On the other hand, samples saturated with oxygen gave neither 2 nor 3 upon irradiation, although prolonged irradiation did produce by-products which caused broad unresolved signals in the nmr spectrum. The fluorescence lifetime of 1 is too short to allow the usual mechanism for oxygen quenching to account for complete destruction of the fluorescent state of this experiment which seems to imply that oxygen prevents formation of both 2 and 3 by quenching triplets. Satisfactory resolution of this problem must await development of a discriminating analytical method suitable for use in direct determination of the quantum yields of 2 and 3 individually. Extensive attempts to find a suitable vapor chromatographic procedure have not yet been successful.

The quantum yield for disappearance of 1 remained constant ($\Phi_p = 0.16$) at least until the reaction was two-thirds complete. Since no product other than 2 and 3 was formed in either the presence or absence of bromocyclopropane, we assume that the total quantum yield (Φ_p) is simply the product of Φ_{isc} and Φ_{tp}. The portion of triplets that go on to products can be calculated: $\Phi_{tp} = 0.6$. Phosphorescence was not observed in an EPA glass at 77°K. The only other thing that can happen to T_1 is radiationless decay, and the quantum yield (Φ_t) for this process must therefore be about 0.4.

The fluorescence quantum yield of 1 was also measured: $\Phi_f = 0.71$. Internal conversion to the ground state is comparatively slow since nearly all of the absorbed light is accounted for by intersystem crossing and fluorescence ($\Phi_f + \Phi_{isc} = 0.96$). Combination of the lifetime data for S_1 with

the quantum yields for fluorescence and intersystem crossing gives estimates for the absolute rates: $k_{isc} = 1.8 \times 10^8$ sec^{-1}, $k_f = 5 \times 10^8$ sec^{-1}.

The rate of fluorescence of naphthalene itself is some 200 times slower[9] than for **1**. This difference occurs because α substituents, especially those containing conjugated unsaturation, shift the short axis-polarized ^1L_a state to lower energy while producing a lesser effect in the long axis-polarized ^1L_b state. This inversion of states along with the allowedness of fluorescence from the ^1L_a state causes **1** to fluoresce much more efficiently than naphthalene. On the other hand, k_f for **1** is about the same as for 1,5- and 1,4-diphenylnaphthalene as well as 1,4,5,8-tetraphenylnaphthalene, all of which have $S_1 = {}^1L_a$.[10]

The unusually fast intersystem crossing rate of **1** as compared with naphthalene ($k_{isc} = 9 \times 10^6$ sec^{-1}) is also a result of the lowest singlet being an ^1L_a state.[11] These states undergo intersystem crossing with more facility due to the difference in electronic configuration. Since the ^1L_b state has nodes at the atoms, spin–orbit coupling is expected to be less effective than in the ^1L_a state which has maximum electron density at the atoms. In contrast to naphthalene, aromatic hydrocarbons with $S_1 = {}^1L_a$ such as anthracene and p-terphenyl have intersystem crossing rate constants of about 10^8 sec^{-1}.[12]

The fluorescent quantum yield of 1,5-divinylnaphthalene (**4**) was determined: $\Phi_f = 0.95$. Since the measured fluorescent lifetime of **4** was 1.4 nsec (the same as for **1**), the maximum intersystem crossing rate for **4** must be less than one-fifth of that measured for **1**. Although the exact numerical relationship of k_{isc} for **1** and **4** is subject to rather large errors, it nevertheless seems clear that the rate is somewhat faster for **1** than for **4**.

4
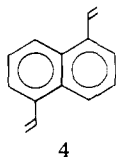
π-Electron SCF-CI calculations[13] suggest that the nodal plnes of the seventh and eight molecular orbitals of **4** are, on the average, closer to the carbon atoms than the nodes of the corresponding orbitals of **1**. i.e., the sum of the magnitudes of the atomic orbital coefficients which contribute to the lowest occupied and highest unoccupied molecular orbitals of **4** is smaller (3.4) than the corresponding sum (4.0) of **1**. Spin–orbit coupling, which depends on electron–nuclei interactions, might be more effective for systems in which the magnitude of the wave functions was higher at the nuclei. Thus, faster intersystem crossing would result for **1**.[14]

Materials

1,5-Divinylnaphthalene (**4**) was prepared as shown in Scheme II. The final step involved a Wittig reaction using dimethyl sulfoxide as solvent and sodium methylsulfinylmethide as base. Compound **1** was synthesized by a similar procedure, and the other materials were acquired as described in the Experimental Section.

Experimental Section

Fluorescence spectra were measured on a Perkin-Elmer MPF-2A spectrofluorimeter. Absorbance measurements were made on a Hitachi Perkin-Elmer Coleman 139 spectrophotometer. The fluorescence lifetimes were determined with a TRW Model 31A nanosecond spectral source (deuterium lamp) coupled to a Tektronix Type 556 dual-beam oscilloscope. Nmr spectra were recorded on a Jeolco PS-100 spectrometer using deuteriochloroform as solvent and tetramethylsilane as internal standard. Benzene was purified by the method of Saltiel.[15] and bromocyclopropane was supplied

Scheme II
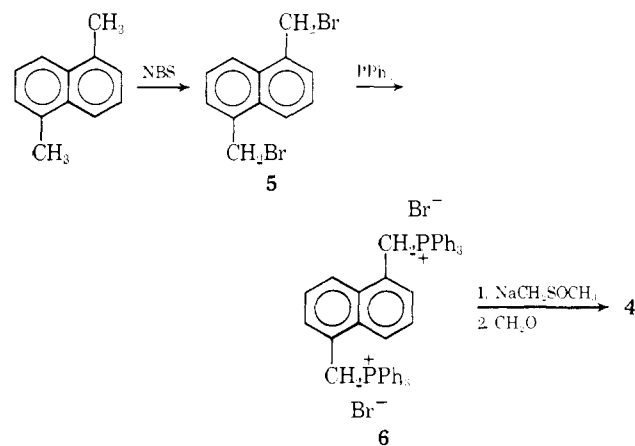
by the Aldrich Chemical Co. and passed through an alumina column just prior to use. Cyclohexane was passed through a silver nitrate–alumina column and fractionally distilled. All samples were degassed by three freeze–pump–thaw cycles to an ultimate pressure of 5×10^{-5} Torr.

1,8-Divinylnaphthalene (1).[16] Crude **1** was prepared by a modification of the method of Mitchell and Sondheimer. It was purified by sublimation, recrystallization (methanol), and resublimation, mp 46.5–47° (lit.[17] mp 47–47.5°).

1,5-Bis(bromomethyl)naphthalene (5).[18] 1,5-Dimethylnaphthalene (5.0 g, 0.0321 mol), N-bromosuccinimide (11.4 g, 0.0642 mol), benzoyl peroxide (0.7 g), and carbon tetrachloride were stirred at reflux for 1 hr. The reaction mixture was concentrated at reduced pressure, and dichloromethane (1 l.) was added. (The product was not soluble in carbon tetrachloride and only slightly soluble in hot chloroform.) The solution was washed with ice water (3 × 300 ml), dried (MgSO$_4$), and concentrated at reduced pressure. The material was sublimed and recrystallized (chloroform) to yield 6.03 g (60%) of product, mp 213° (lit.[18] mp 212°).

1,5-Bis(triphenylphosphoniomethyl)naphthalene Dibromide (6). 1,5-Bis(bromomethyl)naphthalene (5.80 g, 0.0185 mol), triphenylphosphine (9.93 g, 0.0379 mol), and dimethylformamide (50 ml) were heated at reflux for 4 hr and allowed to cool. The solid material was filtered, washed with dimethylformamide (15 ml) and ether (30 ml), and dried *in vacuo* to give product, 14.2 g (92%).

1,5-Divinylnaphthalene (4). Sodium methylsulfinylmethide was prepared from sodium hydride (0.963 g, 0.0402 mol) and dimethyl sulfoxide (100 ml). Bis-phosphonium salt **6** (14.0 g, 0.0167 mol) was added, and the mixture was stirred under inert atmosphere at room temperature for 2.5 hr. Gaseous formaldehyde prepared by heating paraformaldehyde was swept in a slow stream of nitrogen over the surface of the ylide mixture until the orange color had disappeared. After stirring overnight, the mixture was poured into ice water (125 ml). Pentane (125 ml) was added, and the resulting precipitate was filtered and washed with more pentane (4 × 50 ml). The filtrate and washings were combined, and the aqueous phase was removed and washed with more pentane (2 × 100 ml). All the pentane portions were combined, washed with ice water (3 × 125 ml), dried (MgSO$_4$), and filtered through neutral alumina (35 g). Pentane was used to elute the remaining diolefin. Concentration of the eluent under reduced pressure yielded crude product, 2.94 g, mp 56.5–57°. The material was recrystallized (methanol), sublimed, chromatographed over silica gel, and sublimed again, 1.92 g (64%, mp 57° (lit.[19] mp 56°)).

1,4-Diphenylnaphthalene (4). The method of Lepage[20] was used to prepare 1,4-diphenylnaphthalene. The material was recrystallized (ethanol–activated charcoal) to constant melting point and sublimed, mp 134.5° (lit.[20] mp 135°).

Determination of Fluorescence Quantum Yields of 1 and 4.[21] The emission quantum yields in benzene were measured by comparison with 1,4-diphenylnaphthalene in cyclohexane which was assumed to have a quantum yield of 0.40.[22] The samples were prepared with nominal absorbance of 0.5 and diluted tenfold. Fluorescence measurements were made in cylindrical Pyrex cells (13-mm test tubes) with excitation at 313 nm. The indicated quantum yields (0.95 for **4** and 0.71 for **1**) are the results of duplicate sets of measurements which were in excellent agreement with each other. The values

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 × 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 used[24] 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.

References and Notes

(1) Part LXXX: B. Wagner and G. S. Hammond, J. Organometal. Chem., submitted for publication.
(2) G. Ciamician and P. Silber, Ber., **35**, 4128 (1902).
(3) H. Stobbe, Ber., **45**, 3396 (1912).
(4) J. Meinwald and J. W. Young, J. Amer. Chem. Soc., **93**, 725 (1971); J. Meinwald and J. A. Kapecki, ibid., **94**, 6235 (1972); J. Meinwald, J. W. Young, E. J. Walsh, and A. Courtin, Pure Appl. Chem., **24**, 509 (1970).
(5) F. A. Carroll and F. H. Quina, J. Amer. Chem. Soc., **94**, 6246 (1972); see also T. Medinger and F. Wilkinson, Trans. Faraday Soc., **61**, 620

(1965); A. R. Horrocks, A. Kearvell, K. Tickle, and F. Wilkinson, ibid., **62**, 3393 (1966).
(6) For a discussion of approaches to the determination of triplet quantum yields, see J. B. Birks, "Photophysics of Aromatic Molecules," Wiley-Interscience, New York, N.Y., 1970, pp 195–200.
(7) W. A. Pryor, "Free Radicals," McGraw-Hill, New York, N.Y., 1966, pp 99–100.
(8) F. G. Moses, R. S. H. Liu, and B. M. Monroe, Mol. Photochem., **1**, 245 (1969).
(9) I. B. Berlman, "Handbook of Fluorescence Spectra of Aromatic Molecules," Academic Press, New York, N.Y., 1971, p 330.
(10) Reference 9, pp 348, 349, and 351. For a discussion, see pp 72–74.
(11) A. R. Horrocks and F. Wilkinson, Proc. Roy. Soc., Ser. A, **306**, 257 (1968).
(12) See ref 6, pp 286–287 for a compilation of k_{isc} data.
(13) Unpublished results of W. A. Yee and E. M. Evleth, University of California, Santa Cruz.
(14) Horrocks and Wilkinson[11] have suggested a similar argument to rationalize faster intersystem crossing from L_a states than from L_b states.
(15) J. Saltiel and L. Metts, unpublished results.
(16) R. H. Mitchell and F. Sondheimer, Tetrahedron, **24**, 1397 (1968).
(17) J. K. Stille and R. T. Foster, J. Org. Chem., **28**, 2703 (1963).
(18) W. Ried and H. Bodem, Chem. Ber., **91**, 1981 (1958).
(19) R. Stephan, Chem. Ber., **90**, 296 (1957).
(20) Y. Lepage, Bull. Soc. Chim. Fr., 2019 (1963).
(21) See J. N. Demas and G. A. Crosby, J. Phys. Chem., **75**, 991 (1971), for a review of emission quantum yield measurements.
(22) Reference 9, p 348; see also ref 6, pp 103–106, and I. B. Berlman, Chem. Phys. Lett., **22**, 342 (1973).
(23) The emission and excitation slit widths were both 4 nm (narrow band pass conditions), and the absorption spectra of all three compounds were broad and structureless. Thus the measured absorbance was a good indication of the amount of light absorbed in the fluorescence experiment. Since all three compounds had nearly identical emission spectra, a corrected spectrometer was not necessary. The above procedure gave results in satisfactory agreement with literature values for the fluorescence quantum yield of 1,4-bis(dimethylamino)benzene.
(24) C. G. Hatchard and C. A. Parker, Proc. Roy. Soc., Ser. A, **235**, 518 (1956).

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

W. I. Ferree, Jr.,[1] Benjamin F. Plummer,* and W. W. Schloman, Jr.[1]

Contribution from the Chemistry Department, Trinity University, San Antonio, Texas 78284. Received February 26, 1974

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 Drisko[2] 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