Photochemical Heavy-Atom Effect. IV. External and Internal Heavy-Atom Effects upon the Reaction of Acenaphthylene with Cyclopentadiene

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Abstract: The photochemical cycloaddition of acenaphthylene (**1a**) and 5-bromoacenaphthylene (**1b**) to cyclopentadiene (**2**) produces the cycloadducts **3**, **4**, and **5**. These reactions were studied in the solvents cyclohexane, acetonitrile, bromoethane, bromobenzene, 1,2-dibromoethane, and dibromomethane. The triplet nature of each reaction was confirmed by comparison of the product ratios obtained in various solvents in the Rose Bengal sensitized irradiations to the product ratios in the direct irradiations. Good Stern–Volmer relationships were obtained when the quencher ferrocene was used. The quantum yield of product formation has been shown to vary with the concentration of **2** in a manner consistent with a proposed triplet state mechanism. A comparison of the internal and external heavy-atom effect (HAE) upon the various dynamic processes occurring in the acenaphthylene system has been made. It is concluded that the rate processes involved in the radiationless mechanisms $T_1 \leftrightarrow S_1$ and $T_1 \leftrightarrow S_0$ are affected by different degrees when the internal heavy-atom perturbation is compared to the external one. A method is devised to show that relative reactivities of the excited triplet states of **1a** and **1b** are about the same.

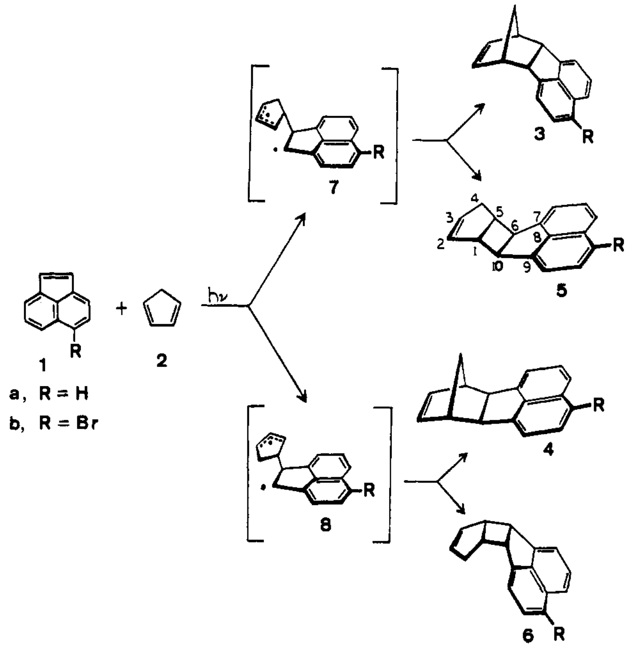
Cowan and Drisko[1] first established that the photodimerization of acenaphthylene (**1a**) was highly sensitive to perturbation by brominated solvents (external heavy atoms). While the effect of heavy atoms on photophysical processes has been thoroughly studied by spectroscopic techniques,[2] known photochemical manifestations are limited.[1,3,4] The ability to enhance product yield or to change product ratios through the heavy-atom effect (HAE) intrigued us. Thus, we reported that acrylonitrile and its derivatives can be cross-cycloadded to **1a** by use of the HAE.[5] This report stimulated others to use the HAE to cross-cycloadd **1a** to maleic anhydride.[6] The synthetic value of the HAE became apparent when the synthesis of pleiadiene was reduced to a four-step procedure involving the HAE.[6a]

Because the requirements for a photochemical HAE remained enigmatic we undertook a detailed study of the photoreaction of **1a** with cyclopentadiene (**2**).[7] Anticipating somewhat different results, we studied the photoaddition of 5-bromoacenaphthylene (**1b**) to **2**.[8] These results appeared in preliminary form and they are discussed in detail in this report with additional data that we have obtained.

Results

A. Structure of Products. Chart I[9] illustrates the three major stereoisomers that have been identified as arising from a photochemical reaction between **1a** and **2** or **1b** and **2**. They are the [4 + 2] products *endo*-7,10-methano-6b,7,10,10a-tetrahydrofluoranthene (**3**), the corresponding exo isomer (**4**), and the [2 + 2] product *exo*-naphtho[1′,8′]tricyclo[3.3.0.0^{6,10}]deca-2,7-diene (**5**). The synthesis of the unsubstituted isomers **3a** and **4a** by a thermal Diels–Alder reaction was recently re-

Chart I



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[1] (a) D. O. Cowan and R. L. Drisko, *Tetrahedron Lett.*, 1255 (1967); (b) *J. Amer. Chem. Soc.*, **89**, 3068 (1967); (c) *ibid.*, **92**, 6281 (1970).

[2] (a) G. A. Giachino and D. R. Kearns, *J. Chem. Phys.*, **52**, 2964 (1970); (b) S. K. Lower and M. A. El-Sayed, *Chem. Rev.*, **66**, 199 (1966); (c) M. A. El-Sayed, *Accounts Chem. Res.*, **1**, 8 (1968); (d) S. P. McGlynn, T. Azumi, and M. Kinoshita, "The Triplet State," Prentice-Hall, Englewood Cliffs, N. J., 1969.

[3] We define a photochemical heavy-atom effect as a change in either quantum yield or product distribution when a given reaction perturbed by a heavy atom is compared to the similar reaction without heavy-atom perturbation.

[4] The following papers have reported photochemical heavy-atom effects in compounds other than acenaphthylene. (a) S. P. Pappas and R. D. Zehr, Jr., *J. Amer. Chem. Soc.*, **93**, 7112 (1971); (b) R. Hoffman, P. Wells, and H. Morrison, *J. Org. Chem.*, **36**, 102 (1971); (c) G. Fischer, K. A. Muszkat, and E. Fischer, *Isr. J. Chem.*, **6**, 965 (1968); (d) F. Wilkinson and J. T. Dubois, *J. Chem. Phys.*, **48**, 2651 (1968).

[5] B. F. Plummer and R. A. Hall, *Chem. Commun.*, 44 (1970).

[6] (a) J. Meinwald, G. E. Samuelson, and M. Ikeda, *J. Amer. Chem. Soc.*, **92**, 7604 (1970); (b) J. E. Shields, D. Gavrilovic, and J. Kopecky, *Tetrahedron Lett.*, 271 (1971); (c) W. Hartmann and H. G. Heine, *Angew. Chem., Int. Ed. Engl.*, **10**, 273 (1971).

[7] B. F. Plummer and D. M. Chihal, *J. Amer. Chem. Soc.*, **93**, 2071 (1971); **94**, 6248 (1972).

[8] B. F. Plummer and W. I. Ferree, Jr., *J. Chem. Soc., Chem. Commun.*, 306 (1972).

[9] To simplify the representation of isomer **5** only one of two positional isomers for the double bond is shown.

ported.[10] We repeated this work and achieved a preparation of white crystalline **3a**,[11] mp 48.4–49.1°, through crystallization from hexane at −78°. Compound **3a** prepared thermally was proved identical with **3a** prepared photochemically through glc, nmr, and mass spectral analysis. Due to the difficulty of achieving a preparative separation, compound **4a** was necessarily analyzed as a mixture with **3a**. Analyses of photoproducts and the Diels–Alder products by standard techniques established that **4a** was identical in both thermal and photochemical product mixtures. Using a computer programmed quadrupole mass spectrometer interfaced with a glc, a complete mass spectral analysis of **3a** and **4a** was obtained. Both isomers show a molecular ion peak at *m/e* 218 with the base peak at 152 (acenaphthylene ion) and a smaller characteristic peak at *m/e* 66 (cyclopentadiene ion). The fragmentation patterns were similar, but showed some differences in the moderate mass regions.

The upfield shift of the nmr vinyl resonance of **3a** at δ 5.3 compared to the vinyl resonance of **4a** at 6.3 ppm is attributable to the position of the hydrogens of **3a** in the diamagnetic anisotropic shielding cone of the aromatic rings.[10,12] This characteristic difference allows easy identification of the two stereoisomers and their substitution products.

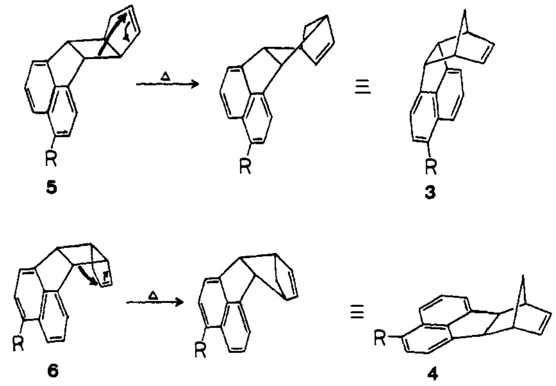
The bromo derivatives **3b** and **4b** were characterized through elemental analysis, mass spectral patterns, and comparison of their nmr spectra to the parent compounds. Compounds **3b** and **4b** gave two nearly equivalent molecular ion peaks *m/e* 298 and 296 that reflected the relative isotopic abundance of the bromine substituent. The base peak at 230 was complimented by a 91% *m/e* peak at 232 (5-bromoacenaphthylene ion) as well as peaks in the mass range 150–153 that indicated loss of bromine. A small peak *m/e* 66 suggesting cyclopentadiene cleavage is consistent with the pattern obtained from the parent hydrocarbons.

The nmr spectrum of **5a** shows the following resonances: δ 2.6 (perturbed doublet, 3 H, allylic), 3.2 (broad singlet, 1 H), 3.8 (m, 2 H, benzylic), 6.0 (m, 2 H, vinylic), and 7.4 ppm (m, 6 H, aromatic). Frequency decoupling experiments were performed. Double irradiation of the hydrogen at δ 3.2 caused the perturbed vinylic peaks to sharpen to an overlapping AB quartet with an apparent $J = 10$ Hz. The allylic and benzylic peaks also showed some perturbations during the measurement. Apparently some long range coupling between H_5 and H_2 and H_3 is occurring. Double irradiation of the three hydrogens resonating at δ 2.6 caused the vinyl peaks to sharpen to an asymmetric pentet while the benzylic hydrogens H_6 and H_{10} sharpened to an apparent AB quartet with $J = 7$ Hz. Double irradiation of the vinyl peaks at δ 6.0 caused the allylic hydrogens at δ 2.6 to sharpen to two overlapping singlets.

The stereochemistry of **5a** has been assigned exo upon the basis of its ready thermal rearrangement to **3a** and its nmr spectrum. The vinylic hydrogens of **5a** that appear at 6.0 ppm are deshielded relative to cyclopentene[13] (δ 5.6) and in comparison to 6-vinylbicyclo[3.2.0]hept-2-ene[14] (δ 5.5, 5.9). The endo isomer of **5a** should reasonably show diamagnetic anisotropic shielding, similar to that found for **3a**. Thus, the available nmr evidence is strongly supportive of exo stereochemistry for **5a**.

Upon heating **5a** to 235° a slow symmetry allowed $[_\sigma2_s + _\pi2_a]$ 1,3-sigmatropic shift to **3a** occurs.[15] This rearrangement further verifies the exo stereochemistry of **5a** because the endo isomer should rearrange to *exo*-**4a** (Chart II).

Chart II



endo-**5a** has not been detected in significant quantities in any of the product mixtures although it has been sought. The absence of appreciable quantities of *endo*-**5a** can be justified upon the basis of the proposed transition states that occur in the photochemical cycloadditions, *vide infra*.

The mass spectral fragmentation pattern of **5a** was clean with a molecular ion peak *m/e* of 218 and base peak at 152 as well as significant peaks at 153, 151, 150, 101, 66, and 39. The mass spectrum of **5a** is very similar to the mass spectra of **3a** and **4a**.

The mass spectrum of **5b** showed molecular ion peaks of *m/e* 298 and 296. Its mass spectrum closely resembled that of stereoisomers **3b** and **4b** (see Experimental Section).

B. Solvent Results. Tables I and II record the results of the photolysis of **1a** and **1b** with **2** (λ >360 nm) in different solvents. The quantum yield for **1a** reacting

Table I. Solvent Dependence for Quantum Yields of Product Formation between Acenaphthylene and Cyclopentadiene[a]

Solvent	ϕ_r[b]	Product ratios[c] 3a	: 4a	: 5a
Cyclohexane	0.0026	0.58	1.46	1.00
Acetonitrile	0.0037	0.78	2.06	1.00
Bromoethane	0.075	0.47	1.36	1.00
Bromobenzene	0.089	0.56	1.42	1.00
1,2-Dibromoethane	0.092	0.50	1.27	1.00
Dibromomethane	0.13	0.50	1.34	1.00

[a] [**2**] = 3.7 *M*; [**1a**] = 0.01 *M*, temperature = 30 ± 5°. [b] Duplicate runs and duplicate analyses for each run. [c] Normalized to the [2 + 2] product **5a**.

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[10] R. Baker and T. J. Mason, *J. Chem. Soc. C*, 596 (1970).

[11] D. M. Chihal, M. S. Thesis, Trinity University, 1970.

[12] J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. 1, Pergamon Press, New York, N. Y., 1965, pp 81–90.

[13] K. B. Wiberg and B. J. Nist, *J. Amer. Chem. Soc.*, 83, 1226 (1961).

[14] G. Sartori, V. Turba, A. Valvassori, and M. Riva, *Tetrahedron Lett.*, 4777 (1966).

[15] R. B. Woodward and R. Hoffman, "The Conservation of Orbital Symmetry," Verlag Chemie, Weinheim Bergstr., Germany, 1970. We thank Professor W. C. Herndon for calling this rearrangement to our attention.

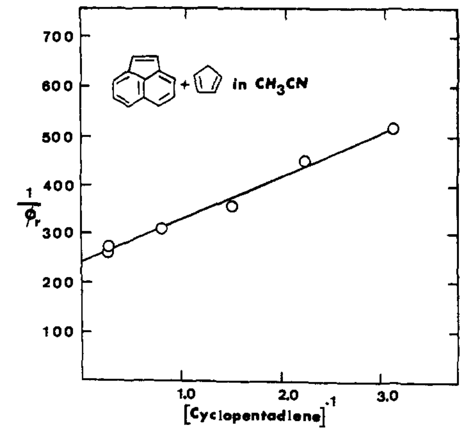

Figure 1. The dependence of ϕ_r upon different concentrations of cyclopentadiene reacting with 0.01 *M* acenaphthylene in acetonitrile.

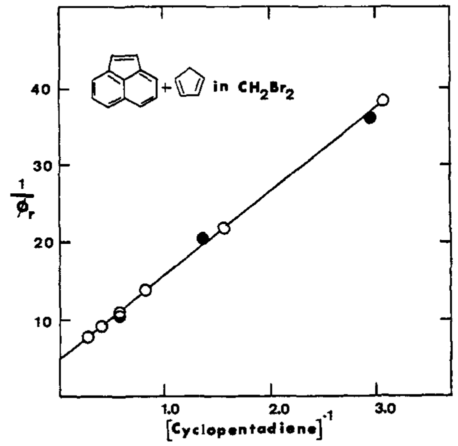

Figure 2. The dependence of ϕ_r upon different concentrations of cyclopentadiene reacting with 0.01 *M* acenaphthylene in dibromomethane: (●) different concentrations of CH_2Br_2; (○) constant concentration of CH_2Br_2.

Table II. Solvent Dependence for Quantum Yields of Product Formation between 5-Bromoacenaphthylene and Cyclopentadiene[a]

Solvent	ϕ_r	Product ratios 3b	: 4b	: 5b
Cyclohexane	0.016	0.53	1.93	1
Acetonitrile	0.020	0.66	3.01	1
Bromoethane	0.020	0.60	2.03	1
Bromobenzene	0.026	0.55	1.68	1
1,2-Dibromoethane	0.028	0.64	1.74	1
Dibromomethane	0.029	0.53	1.66	1
Iodomethane	0.021	0.62	1.44	1

[a] All concentrations and conditions are the same as described in Table I.

with **2** increases 50-fold in dibromomethane when compared to cyclohexane. In accord with earlier results[1] a greater HAE is found for the solvents containing a greater proportion of bromine. The relative product ratios in most solvents for **1a** reacting with **2** are reasonably constant although acetonitrile deviates.

Compound **1b** reacting with **2** shows quite different solvent effects. There is less than a factor of 2 difference for the quantum yield of reaction upon progressing from cyclohexane to dibromomethane. Compound **1b** shows about a sevenfold greater quantum yield in cyclohexane than does **1a** under identical conditions. It is significant that iodomethane shows no greater effect on the quantum yield for **1b** reacting with **2** than does bromoethane. The product ratios for cycloaddition of **1b** to **2** are reasonably consistent although acetonitrile is found to produce a greater proportion of the exo [4 + 2] product.

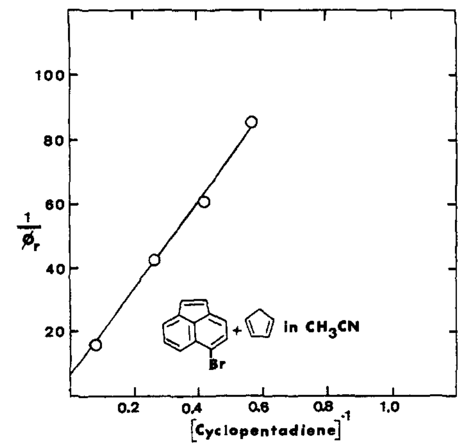

Figure 3. The dependence of ϕ_r upon different concentrations of cyclopentadiene reacting with 0.01 *M* 5-bromoacenaphthylene in acetonitrile.

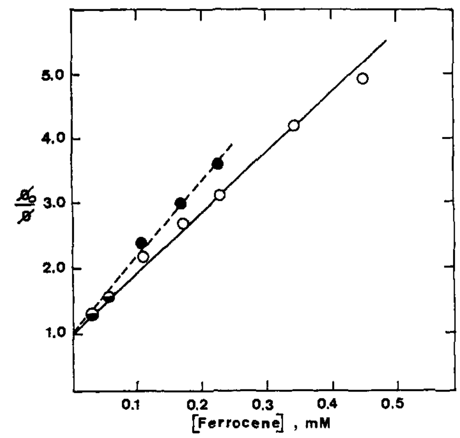

Figure 4. A typical Stern–Volmer plot of the reaction between acenaphthylene and cyclopentadiene as a function of the concentration of ferrocene quencher: (●) 0.65 *M* in cyclopentadiene; (○) 3.7 *M* in cyclopentadiene.

Figures 1–3 illustrate the effects of solvent and of varying the concentration of **2** in separate reactions with **1a** and **1b**. A linear relation is found between the reciprocal of ϕ_r and the reciprocal of the cyclopentadiene concentration. In Figure 2, the solid dots represent runs in which the sample volume was kept constant by increasing the amount of CH_2Br_2 as the volume of **2** was decreased. The open circles represent experiments in which the concentration of CH_2Br_2 was held constant by adding the required amount of cyclohexane to maintain volume as the amount of **2** was decreased. Thus, the data indicate that the concentrations of heavy-atom solvents studied here are not in a range that is critical to the other measurements.

C. Quenching Results. Figure 4 illustrates a typical Stern–Volmer plot of the results of the ferrocene quenching of the reaction between 0.01 *M* **1a** and two concentrations of **2**. In 3.7 *M* **2** the quenching dependence varies linearly with ferrocene up to 80% quenched reaction. The data obtained from other quenchers are reported in Table III. Cyclooctatetraene, ferrocene, di-*tert*-butyl nitroxide, and oxygen were studied. A high degree of variability was encountered, although ferrocene and cyclooctatetraene were efficient quenchers of the cycloaddition of **1** to **2**. Table IV summarizes the results obtained from ferrocene quenching studies of separate reactions between **1a** and **2** and **1b** and **2**.

Table III. Quenching Data for Reactions of 0.01 *M* Acenaphthylene and 5-Bromoacenaphthylene Reacting with Cyclopentadiene

Compd	Solvent	Quencher (M)	[**2**]	Quantum yield[a]	% quenched
1a	CH_3CN	O_2[b]	0.66	0.0033	10
1a	CH_3CN	COT[c] (1.9×10^{-2})	0.66	0.00003	97
1a	CH_3CN	DTBN[c] (1.9×10^{-2})	0.66	0.0026	30
1b	CH_2Br_2	O_2[b]	3.7	0.027	5

[a] Based on product formation. [b] Concentration assumed to be very low (see Discussion). [c] COT = cyclooctatetraene; DTBN = di-*tert*-butyl nitroxide.

Table IV. Rates and Intersystem Crossing Yields from Quenching and Concentration Dependence Data[a]

Compd	Acenaphthylene		5-Bromoacenaphthylene
Solvent	CH_3CN	CH_2Br_2	CH_3CN
	Concentration Dependence		
Slope, M^{-1}	86.8 ± 4.6	10.76 ± 0.09	142.7 ± 4.6
Intercept	241 ± 8	4.90 ± 0.13	4.59 ± 1.75[b]
Correlation	0.994	0.999	0.999
	Ferrocene Quenching[c]		
Slope, M^{-1}	$29{,}100 \pm 2300$	8410 ± 270	2040 ± 220
	Values Derived		
$\alpha\phi_{isc}$	0.0042	0.21	0.22
k_d/k_r	0.36	2.2	31
k_r[d]	3.4	3.0	6.8
k_d[d]	1.22	6.6	214

[a] Parameters derived by least-squares treatment of data treated according to eq 9 and 10. [b] The short triplet lifetime of **1b** produces a large slope and this leads to a large relative error in the small intercept. [c] Cyclopentadiene concentration was 3.7 *M*. [d] In units of 10^4 sec^{-1}, calculated from assumed values for k_q (see text).

D. Sensitized Photocycloadditions. The data for the dye-sensitized photoaddition of **1a** and **1b** to **2** using Rose Bengal and the 589-nm light from a sodium lamp are presented in Table V. We desired to study the sensitized product distribution in solvent systems that were identical with the mixtures used in direct irradiations. This was not possible because the sodium salt of Rose Bengal is not soluble in hydrocarbon solvents. The dicyclohexyl-18-crown-6-ether complex[16] of the disodium salt of Rose Bengal was prepared and found to be sufficiently soluble in hydrocarbon solvents to be used as a sensitizer. Its visible and ultraviolet spectra in hydrocarbon solvents were similar to aqueous solutions of the uncomplexed dye, but showed a bathochromic shift. The crown ether complex of the dye showed a disconcerting tendency to photobleach in dilute solution.[17] Saturated hydrocarbon solutions of the complex would slowly aggregate and precipitate with time. These conditions were ameliorated by the addition of a small quantity of methanol. No precipitation occurred nor did the complex photobleach during the sensitized runs.

Table V. Rose Bengal Sensitized Photoaddition of **1a** and **1b** to **2** at 589 nm[a]

Compound	Solvent	Product ratio **3**	:	**4**	:	**5**
1a	CH_3CN	0.66		1.92		1
1a	CH_2Br_2	0.54		1.32		1
1b	CH_3CN	0.89		3.24		1
1b	CH_2Br_2	0.93		1.84		1

[a] Crown ether complex of dye used; [**2**] = 3.7 *M*.

The product ratios in the sensitized runs are similar to those that result from direct irradiations. The solvent compositions are not identical (10% methanol in the sensitized runs) so that the sensitized ratios probably reflect some solvent influence.

Discussion

The Triplet State. The triplet nature of the reactions of acenaphthylene and 5-bromoacenaphthylene with cyclopentadiene is indicated by the fact that the product ratios found for the direct and sensitized photolyses are very similar and exhibit similar effects of solvent polarity (Tables I, II, and V). Previous studies have shown that Rose Bengal[1c,18] fits the criteria of a triplet sensitizer toward acenaphthylene and that energy transfer from Rose Bengal (E_T = 44.6 kcal)[1c] to acenaphthylene [E_T about 40 kcal)[1c,18] is probably exothermic. Fluorenone (E_T = 53.3 kcal)[19] sensitizes the addition of **1a** to **2** and also gives product ratios similar to those found in the other reactions. However, fluorenone has several complications that make it less desirable as a triplet sensitizer for this study.[20]

The unsensitized reactions are quenchable by cyclooctatetraene (E_T assumed to be less than 39 kcal)[18] or ferrocene (E_T = 40.2 kcal).[21,22] Previous studies of the photodimerization of **1a**[1a,18] have shown that these quenchers effectively quench the excited triplet of **1a**.

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(16) C. J. Pederson and H. K. Frensdorf, *Angew. Chem.*, **84**, 16 (1972).

(17) We are investigating the sensitizing properties and photochemistry of crown ether complexes of various dyes.

(18) I. M. Hartmann, W. Hartmann, and G. O. Schenck, *Chem. Ber.*, **100**, 3146 (1967).

(19) W. G. Herkstroeter, A. A. Lamola, and G. S. Hammond, *J. Amer. Chem. Soc.*, **86**, 4537 (1964).

(20) Unpublished data of Dr. W. I. Ferree. Fluorenone has a transmission band in the visible that is quite similar to **1a**. Thus high concentrations of fluorenone are needed to absorb a significant fraction of the light. Further, **2** quenches some fluorenone singlets before they cross to the triplet. Preliminary actinometric studies of the fluorenone sensitized cycloaddition of **1a** to **2** suggest that after corrections for light absorption by **1a** and singlet quenching of fluorenone by **2** the sensitized quantum yield of **1a** to **2** is about 0.25. This value is used to estimate the value for the parameter α, *vide infra*.

(21) J. P. Guillory, C. F. Cook, and D. R. Scott, *J. Amer. Chem. Soc.*, **89**, 6776 (1967).

(22) A referee has commented that there may be some singlet quenching occurring at the concentrations of quenchers used here (about 0.02 *M*). We doubt there is significant singlet quenching because the cis photodimer that arises from the excited singlet state of **1a** can be produced by irradiating an oxygen saturated solution (about 0.02 *M*) of **1a**.[1c] This implies that the singlet lifetime of **1a** is short (which our data corroborates) and that a very high concentration of quencher will be needed to achieve significant singlet quenching of **1a**.

The absence of efficient quenching by either oxygen or di-*tert*-butyl nitroxide for reaction between **1a** and **2** was unexpected. However, we find that solutions saturated with pure oxygen will not measurably quench the fluorescence of naphthalene when cyclopentadiene is present. Since oxygen is reported[23] to react with **2** at 25°, we attribute the absence of oxygen quenching to its consumption by **2** in our reaction mixtures. The low quenching efficiency of di-*tert*-butyl nitroxide may be due to a low k_q[24] or to its reaction with **2**. Caldwell and Schwerzel[24] recently reported that di-*tert*-butyl nitroxide has a k_q of about 5×10^8 M^{-1} sec^{-1} for quenching triplets of aromatic hydocarbons. This is not low enough to explain our data. The fact that nitric oxide readily consumes **2**[25] suggests to us that di-*tert*-butyl nitroxide may be scavenged by **2** and thus the effective nitroxide concentration is reduced in the mixture.

Proposed Mechanism. A mechanism consistent with our observations is shown in Chart III, where A is **1a** or **1b**, C is **2**, Q is quencher, I is intermediate diradical, 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, diradical formation, diradical disproportionation, and the rate constant for product formation from [I]. We define α as the ratio $k_T/(k_{-r} + k_T)$. Thus, if α were unity all diradicals would yield product.

Chart III

	Rate	
$A \xrightarrow{h\nu} {}^1A$	I_a	(1)
${}^1A \xrightarrow{k_{ic}} A$	$k_{ic}[{}^1A]$	(2)
${}^1A \xrightarrow{k_{isc}} {}^3A$	$k_{isc}[{}^1A]$	(3)
${}^3A \xrightarrow{k_d} A$	$k_d[{}^3A]$	(4)
${}^3A + Q \xrightarrow{k_q} A + {}^3Q$	$k_q[{}^3A][Q]$	(5)
${}^3A + C \xrightarrow{k_r} [I]$	$k_r[{}^3A][C]$	(6)
$[I] \xrightarrow{k_{-r}} A + C$	$k_{-r}[I]$	(7)
$[I] \xrightarrow{k_T}$ products	$k_T[I]$	(8)

Previous studies have shown that acenaphthylene emits negligible fluorescence or phosphorescence under the most favorable conditions.[26] Thus, these degradation steps are not included in the mechanistic scheme. Absorption of light to form directly excited triplet **1** is excluded for similar reasons.[1,2a] Therefore, the minimal mechanism shown is assumed to be adequate.[8] By application of the steady-state assumption, eq 9 is derived for the quantum yield of reaction, ϕ_r. Observing that the first term in parentheses in eq 9 is the

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

quantum yield of intersystem crossing, ϕ_{isc},[27] and further simplifying by setting the term $k_q[Q]$ equal to zero, the reciprocal of eq 9 appears as eq 10. Figures 1–3 corroborate the fit of our data to eq 10 with good correlation coefficients ($r > 0.99$). From the reciprocals of the intercepts of these plots, $\alpha\phi_{isc}$ in each solvent may be obtained and the slope divided by the intercept will yield values of k_d/k_r (Table IV).

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

A complication to the proposed mechanism is singlet quenching of **1** by **2**, as is observed for many aromatic hydrocarbons.[28] If this were to occur to an appreciable extent, plots of $1/\phi_r$ against $1/[\mathbf{2}]$ would curve considerably. This is not observed. We believe that the absence of significant singlet quenching is attributable to the extremely short singlet lifetime of **1**[22] as is suggested by its minimal fluorescence yield.

Interpretation of $\alpha\phi_{isc}$. The interpretation of the reciprocal of the intercept involves determining the value to be used for α, the fraction of triplet diradical intermediates that yield product, and the value to use for ϕ_{isc}. Data from fluorenone sensitization of the addition of **1a** to **2**[20] suggest that for purposes of discussion the assumption that ϕ_{isc} is about 1.00 in heavy-atom solvents will be reasonably valid. This assumption causes the minimum value of α to be about 0.2. The inefficiency of the triplet reaction thus arises from a high percentage of disproportionation of the intermediate back to ground-state molecules. Similar inefficient triplet reactions have been observed. The photodimerization of cyclopentenone where ϕ_{isc} is 1.0 has been shown to be quite inefficient and α in that system is about 0.3.[29] The sensitized dimerization of triplet indene has also shown a high degree of inefficiency. In this system α appears to be about 0.2.[30] DeBoer concludes that dissociation of indene triplet excimers is the energy-wasting step. Because of the large relative energy differences between the triplet states of **2**[31] and **1a** or **1b** we doubt that decay to ground-state molecules *via* an exciplex is the energy-wasting step in our system. We currently favor the dissociation of the triplet diradical intermediate to ground-state molecules as the energy-wasting step.

In acetonitrile we find the value for $\alpha\phi_{isc}$ for **1a** reacting with **2** to be 0.0042. A minimum value of 0.2 for α suggests that the upper limit for ϕ_{isc} of **1a** in non-heavy-atom solvents is about 0.02. The absence of observable phosphorescence for acenaphthylene suggests that in non-heavy-atom solvents ϕ_{isc} is even lower than 0.02.

Quenching Data. The Stern–Volmer quenching slope for the proposed mechanism is expressed as eq 11. The k_d/k_r values from eq 10 may thus be inserted into eq 11

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[23] H. Hock and F. Sepke, *Chem. Ber.*, 84, 349 (1951).

[24] R. E. Schwerzel and R. A. Caldwell, *J. Amer. Chem. Soc.*, **95**, 1382 (1973).

[25] N. V. Stanicarbon, British Patent 917,023 (1960); *Chem. Abstr.*, **58**, 8678c (1963).

[26] (a) R. Livingston and K. S. Wei, *J. Phys. Chem.*, 71, 541 (1967); (b) E. Heilbronner, J. P. Weber, J. Michl, and R. Zahradnik, *Theor. Chim. Acta*, **6**, 141 (1966); (c) A. Bree, C. Y. Fan, and R. A. Kydd, *Spectrochim. Acta, Part A*, **25**, 1375 (1969); (d) we have also studied the emission of **1** in methylene bromide at 77°K and found that no phosphorescence was observed under conditions where an estimated quantum yield of phosphorescence of 0.03 should have been detectable.

[27] N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, New York, N. Y., 1967, p 130.

[28] D. A. Labianca, G. N. Taylor, and G. S. Hammond, *J. Amer. Chem. Soc.*, **94**, 3679 (1972), and references cited therein.

[29] P. J. Wagner and D. J. Bucheck, *J. Amer. Chem. Soc.*, **91**, 5090 (1969).

[30] C. DeBoer, *J. Amer. Chem. Soc.*, **91**, 1855 (1969).

[31] The E_T of cyclopentadiene is reported to be 58.3 kcal/mol: D. F. Evans, *J. Chem. Soc.*, 1735 (1960).

$$\frac{(\phi_r)_0/\phi_r - 1}{[Q]} = \frac{k_q}{k_r[C] + k_d} \qquad (11)$$

to calculate individual values of k_r and k_d that are dependent only on the value chosen for k_q. Recent reports suggest[32] that k_q for ferrocene is in the range of 2.4–7.0 × 10^9 M^{-1} sec^{-1}. Choosing $k_q = 4 \times 10^9$ M^{-1} sec^{-1} for both compounds in acetonitrile, and assuming k_q is reduced in methylene bromide in proportion to the ratio of viscosities of the two solvents[33] to 1.5 × 10^9 M^{-1} sec^{-1}, the vaues for k_r and k_d in Table IV are estimated. The values of k_r thus obtained are nearly constant while k_d is increased progressively as external or internal perturbation is applied to **1a**.

It is recognized that if k_q for ferrocene quenching of **1b** is less than that for quenching of **1a**, k_d and k_r for **1b** will be overestimated proportionately. In addition, the large relative uncertainty in the concentration dependence intercept for **1b** indicates the $\alpha\phi_{isc}$ and rate constants derived for this compound are very approximate values. However, the lowest value of k_d/k_r, within the standard deviations of the concentration dependence data for **1b**, is 16. If k_r of **1b** is assumed to be at least 3 × 10^4, as it is for **1a** in the two solvents, we compute a probable minimum value for k_d as 48 × 10^4, which is still seven times that of **1a** under external heavy-atom perturbation. We, therefore, feel that the data derived for **1b** in Table IV are fair estimates and that the comparisons to follow are essentially independent of experimental uncertainty or assumptions about k_q.

Comparison of Derived Constants. Variations in the values of $\alpha\phi_{isc}$ and k_d alone completely account for the response of ϕ_r to the internal and external HAE. For the reaction of acenaphthylene with 3.7 *M* cyclopentadiene, ϕ_r and $\alpha\phi_{isc}$ are nearly equal. Therefore, k_d, the excited triplet decay constant, is not competitive with the term k_r[C], the product of the excited triplet bimolecular rate constant and the concentration of **2**. We conclude that in 3.7 *M* **2** in acetonitrile nearly all triplets formed produce intermediates, the low ϕ_r resulting from a small value of ϕ_{isc} and a small value for α. When the solvent is changed to methylene bromide, the external HAE produces a ϕ_{isc} close to unity (if k_{ic}, the internal conversion rate constant is unaffected,[35] the minimum increase in k_{isc} is by a factor of 50) and the opposing decrease in k_d is only by fivefold, allowing ϕ_r to increase by a large factor of 35. The difference between ϕ_r of 0.13 and $\alpha\phi_{isc}$ of 0.21 in the solvent CH_2Br_2 illustrates how radiationless decay of excited triplet **1a** has become competitive with formation of the intermediates that lead to product.

The data for reaction of 5-bromoacenaphthylene with 3.7 *M* cyclopentadiene in acetonitrile show that k_d as well as $\alpha\phi_{isc}$ exhibit a large increase as a result of the internal HAE. While $\alpha\phi_{isc}$ for **1b** in acetonitrile is similar to that for **1a** in methylene bromide, k_d is larger by a factor of about 30 for the internal heavy-atom perturbation. This shortens the triplet lifetime of **1b** and therefore accounts for the low ϕ_r of **1b**. It also supports our contention[8] that the internal HAE on the rates k_d and k_{isc} is by different relative proportions than the external HAE on these rates, the internal effect on k_d being relatively larger.

Submitting the reaction of **1b** with **2** to additional heavy-atom effects externally results in slightly increased values of ϕ_r. This is consistent with the supposition that the external HAE on k_d is small as compared to further increases in k_{isc} to nearly maximize ϕ_{isc}. A saturation effect appears likely since, according to eq 9, k_d cannot be increased further by a factor larger than 2 without causing ϕ_r to decrease rather than increase (as is observed) with additional external perturbation. The fact that the best heavy-atom perturber solvent, CH_3I, has no greater effect upon ϕ_r for **1b** than the brominated solvents adds credence to this assumption.

We conclude that heavy-atom effects in the reactions of acenaphthylene or 5-bromoacenaphthylene with cyclopentadiene are best explained as due to specific perturbations that affect ϕ_{isc} and k_d. This differs from reported heavy-atom effects on phosphorescence, where the rate of triplet emission, k_p, is increased concomitant with ϕ_{isc} and k_d.[2a] Our study suggests that k_r, the rate of reaction of excited triplet **1a** or **1b** with substrate, is barely affected by heavy atoms. Thus, HAE on reaction quantum yields in general are likely to be much smaller than those on phosphorescence yields.

The data reported here are based upon a kinetic–product study rather than a spectroscopic approach. It is therefore gratifying to find that this study reinforces the view obtained from spectroscopic measurements that internal and external heavy-atom effects on the processes $S_1 \rightarrow T_1$ and $T_1 \rightarrow S_0$ may be characterized by different mechanisms.[2c]

Product Ratios. The product ratios in Tables I and II are indicative of the photochemical nature of these reactions. The thermal Diels–Alder reaction requires temperatures of 175° and produces only [4 + 2] products in an endo/exo ratio of 3:1.[10] The photochemical reaction produces quite different product ratios and also yields the exo [2 + 2] product **5**. Chart I summarizes possible intermediates that lead to the products observed. The proposed diradical intermediates may partition among the various products through rotation about the first formed bond. The direction of rotation most favored would yield the major product from that intermediate. Thus, the fact that exo [4 + 2] product **4** is the major one suggests that diradical **8** rarely proceeds to form endo [2 + 2] product **6**, and this is consistent with considerations of steric hindrance. It is also supported by the fact that we have not been able to detect by glc any quantity of **6**. Diradical **7** produces the endo [4 + 2] and exo [2 + 2] isomers. If steric hindrance to bond rotation in the intermediate diradical is important, then we predict that the exo [2 + 2] isomer should predominate. The data (Tables I and II) corroborate this assumption.

We note with interest that the product ratios are

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[32] (a) A. J. Fry, R. S. H. Liu, and G. S. Hammond, *J. Amer. Chem. Soc.*, 88, 4781 (1966); (b) R. B. Cundall, G. B. Evans, and E. J. Land, *J. Phys. Chem.*, 73, 3982 (1969).

[33] At 30° the viscosities of methylene bromide and acetonitrile are respectively 0.92 and 0.345 cP.[34]

[34] J. Timmermans and Mme. Hennault-Roland, *J. Chim. Phys. Physicochim. Biol.*, 27, 401 (1930); **29**, 529 (1932).

[35] The bulk of evidence suggests that heavy-atom effects are most profound on intersystem crossing,[2d] but an effect on internal conversion has been proposed: L. S. Forster and D. Dudley, *J. Phys. Chem.*, **66**, 838 (1962).

different in cyclohexane and acetonitrile. That there is a polarity effect upon product distribution in these reactions is not surprising, because Schenck, *et al.*,[18] found that the sensitized photodimerization of **1a** follows a Kirkwood–Onsager plot for solvent dielectric. The difficulty of interpretation lies in assessing the importance of solvent on the transition states leading to the diradicals and upon the partitioning of the diradicals to products or to ground-state molecules.

It is conceivable that each photoproduct is derived from a separate transition state.[36] We anticipate that further solvent studies may clarify this point.

Summary and Prognosis

We have shown that the acenaphthylene system is well suited for the examination of internal and external heavy-atom effects. Perturbation by bromine either internally or externally can increase $S_1 \rightarrow T_1$ intersystem crossing by comparable amounts, but the effect on $T_1 \rightarrow S_0$ radiationless decay is much larger with internal bromine. The reactivities of the excited triplets of **1a** and **1b** are comparable and relatively unimportant in accounting for the differences in quantum yields of reaction.

The method used herein for measuring the value of ϕ_{isc} may be applicable to other compounds that undergo triplet cycloadditions provided that singlet quenching is taken into account, and that it can be assumed or shown what fraction of intermediate diradicals fragment to ground-state starting materials. A similar approach to measurements in the gas phase has recently appeared.[37]

The ability to increase a reaction quantum yield by heavy-atom perturbation appears to be susceptible to saturation. Thus, **1b** with ϕ_{isc} near 1.00 shows small effects on reactivity from external heavy atoms. However, **1a** with ϕ_{isc} of less than 0.02 is extremely sensitive to external heavy-atom perturbation. It seems likely that future investigators seeking other molecular species susceptible to the photochemical heavy-atom effect will first need to know that ϕ_{isc} is very low for the compound. If this is true and the energy constraints are proper[2a] then the molecule may manifest a heavy-atom effect in photochemical reactions.

Experimental Section

Materials. Acenaphthylene (Aldrich, Tech.) was purified by the dimer cleavage method[26a] or by recrystallization of the picrate complex.[18] Ferrocene (Eastman practical) was recrystallized twice from hexane and sublimed. *trans*-Stilbene (Aldrich) was used as received and contained 0.55% *cis*-stilbene by glc analysis. Benzylnaphthalene was synthesized,[38] sublimed, and recrystallized from ethanol. Benzophenone (Eastman, White Label) was recrystallized from absolute ethanol. Benzil (Eastman, White Label) was recrystallized from ligroine (bp 65–90°). Di-*tert*-butyl nitroxide was prepared according to the method of Hoffman and Henderson.[39]

Solvents were Aldrich White Label grade and were routinely dried over Linde 5A Molecular Sieves and freshly distilled through a 1-m Vigreux fractionating column. Benzene (Eastman Reagent) was distilled from CaH_2. Cyclopentadiene was obtained by freshly cracking dicyclopentadiene (Aldrich) and distilling slowly through a 0.1-m Vigreux column.

Instrumentation. Glc analyses were performed with a Varian 1200 Hi-Fl with a Sargent SR recorder equipped with Disc integrator. Column A was a 7 ft × 0.125 in. 3% OV-17 on 80–100 mesh Chromosorb W. Column B was a 4 ft × 0.125 in. 3% OV-1 on 80–100 mesh Chromosorb W. Preparative scale separations were achieved using a Varian 920 glc. Infrared spectra were obtained as thin films or in KBr pellets on a Perkin-Elmer 337 spectrometer. Ultraviolet measurements were obtained from a Beckman DU-2 or DB-G recording spectrophotometer. Precise quantum yield determinations were obtained using a Bausch and Lomb 33-86-07 uv–visible monochromator with 150-W xenon lamp. Fluorescence and phosphorescence measurements were obtained from an Aminco Bowman spectrophotofluorimeter. A Varian T-60 nmr spectrometer equipped with frequency decoupler was used to obtain nmr spectra from dilute solutions (1–10%) of solute dissolved in $CDCl_3$ or CCl_4 at 34°. A Finnegan 1015C System/150 computer controlled ensemble 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 **1a** were performed with a 450-W Hanovia lamp housed in a quartz immersion well with circulating cold copper nitrate (0.7 *M*) solution to remove wavelengths of light shorter than 360 nm. The lamp was placed in the center of a Rayonet MGR-500 merry-go-round apparatus contained in a hood 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 **1a** was always larger than 3.0 after cessation of the reaction.

Direct irradiations of solutions of **1b** were performed in a Rayonet RPR-100 reactor with attached merry-go-round apparatus and 3500-Å lamps (band width 310–410 nm).

Sensitized irradiations were performed with a Sargent-Welch sodium vapor lamp placed at the center of a Rayonet photochemical reactor. The photolyses tubes were suspended around the lamp by use of a MGR-100 merry-go-round reactor.

Calibrated Pyrex tubes (Rayonet RPV-8) were filled to 15.0-ml marks with mixtures to be irradiated. An additional 0.2 ml of solvent was added to each tube to replace that which would be volatilized during the deoxygenation procedure. Oxygen was removed from each mixture by a 30 min purge with nitrogen gas that had undergone prior passage through a concentrated H_2SO_4 trap and several solid KOH traps; then each tube was quickly stoppered and irradiated. Irradiation times varied from about 2 min (**1a** in CH_2Br_2 solvent) to about 1 hr (**1a** in CH_3CN solvent). After irradiation weighed aliquots of solutions of the requisite internal standard, *vide infra*, were added and the tubes were analyzed.

Analyses. Photolysis mixtures containing products derived from **1a** were analyzed on column A at 158°. Internal standards were acenaphthene and 5-bromoacenaphthene for unreacted **1a** and compounds **3a**, **4a**, and **5a**, respectively. Similarly, products derived from **1b** were analyzed on column B at 160°. The internal standard for unreacted **1b** was 5-bromoacenaphthene and the internal standard for compounds **3b**, **4b**, and **5b** was α-benzylnaphthalene. Because of the short retention times, unreacted **1a** or **1b** was analyzed by relative peak height to the corresponding internal standard and corrected by standardized plots for any difference in detector response. The analysis of cycloadducts **3**, **4**, and **5** was by Disc integration of peak areas relative to the internal standard. Computer programs were used to analyze the data and to correct the areas for base-line drift and detector response. Most measurements were obtained on duplicate samples, each being analyzed twice.

Standard samples of all cycloadducts were passed through the columns at various temperatures to ensure that the temperatures chosen for analysis were not causing measurable thermal rearrangement of the cycloadducts.

Actinometry. It was experimentally verified that a 0.1 *M* benzil solution gave a transmission spectrum nearly congruent with a 0.01 *M* solution of acenaphthylene between 360 and 480 nm, the wavelength of 100% transmittance. Thus, the benzil (0.1 *M*) sensitized isomerization of *trans*-stilbene in benzene was used as the actinom-

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(36) It has been proposed that most biradical mechanisms are better replaced by concerted mechanisms: N. D. Epiotis, *J. Amer. Chem. Soc.*, **94**, 1941 (1972).

(37) S. H. Jones and T. L. Brewer, *J. Amer. Chem. Soc.*, **94**, 6310 (1972).

(38) C. D. Nenitzescu, D. A. Isacescu, and C. N. Ionescu, *Justus Liebigs Ann. Chem.*, **491**, 217 (1931).

(39) A. K. Hoffman and A. T. Henderson, *J. Amer. Chem. Soc.*, **83**, 4671 (1961).

eter[40] with correction for back isomerization.[41] The quantum yield for the benzil sensitized isomerization of 0.05 *M trans*-stilbene was determined to be 0.437 by comparison to the benzophenone sensitized isomerization of 0.05 *M trans*-stilbene with a quantum yield of 0.450.[41] For longer irradiation times, it was necessary to increase the concentration of *trans*-stilbene from 0.05 to 0.15 *M*. This caused the experimental isomerization quantum yield to decrease to 0.415. The quantum yields for the actinometers were determined on a Bausch and Lomb monochromator at 366 ± 12 nm.

Because the transmission spectrum of 5-bromoacenaphthylene did not correspond closely to that of benzil, the quantum yield determinations for **1b** were performed by irradiating solutions of **1b** in parallel with solutions of **1a** reacting with **2** in CH_2Br_2 as the actinometer using the Rayonet reactor with 3500-Å lights. Both **1a** and **1b** absorb all the light emitted from these sources.

Of the quenchers used, dilute solutions of cyclooctatetraene are completely transparent above 300 nm.[42] Although ferrocene is yellow, it has a transmittance window at 366 nm ($\epsilon \simeq 10$),[43] whereas 0.01 *M* **1a** and **1b** both have large absorbances at this wavelength ($A > 7.0$). The concentration of ferrocene would have to exceed 0.7 *M* before it could begin to competitively quench the reactions by physical light absorption. Di-*tert*-butyl nitroxide has a weak absorption at 465 nm ($\epsilon \simeq 10$) and only end absorption at 300 nm.[39] At 366 nm solutions of di-*tert*-butyl nitroxide are also essentially transparent. Oxygen quenching was performed by passing a slow stream of pure oxygen through the various solutions for 30 min.

All of the heavy-atom solvents used in this study are essentially transparent to light of wavelengths greater than 320 nm.[44] No evidence was found that any HBr was photochemically or thermally produced in the purified solvents during the short times these solvents were subjected to irradiation.

The adducts **3**, **4**, and **5** do not absorb significantly above 310 nm and were shown to be inert to light of the wavelengths used in this study.

Material Balance. Production of **3**, **4**, and **5** accounts for about 90% of the disappearance of **1a** or **1b** when **2** is 3.7 *M*. As the concentration of **2** is lowered, the difference between quantum yields of product formation and consumed starting material remains approximately constant and, thus, product formation accounts for a smaller proportion of disappeared starting material. For example, when **2** is 0.66 *M* in acetonitrile or methylene bromide detected products account for about 60% of consumed **1a**. Triplet quenchers affect only that portion of the disappearance of starting material that is attributable to product formation. No products other than those reported can be detected by glc suggesting that dimers or oligimers formed from **1** are responsible for the discrepancy.

5-Bromoacenaphthylene (1b). 5-Bromoacenaphthene (Aldrich) (5.9 g, 25 mmol) was brominated with *N*-bromosuccinimide,[45] followed by dehydrobromination with lithium chloride in dimethylformamide[46] to yield after recrystallization from methanol, 1.7 g (7.4 mmol, 30%) of **1b**, mp 53–54°. Sublimation (50° (0.03 mm)) was repeated until the only detectable impurity by glc (column B) was 3.5% 5-bromoacenaphthene: mp 55–56.5°; nmr δ (CCl_4) 6.85 (s, 2 H), 7.2–8.0 ppm (m, 5 H, aromatic); ir (KBr) 3100, 3070, 3030, 1480, 1420, 1380, 1360, 1210, 1168, 1082, 1071, 1028, 1019, 881, 720–640, 527 cm^{-1}; uv $\lambda_{max}^{cyclohexane}$ 243 nm (ε 14,000), 329 (10,900), 344 (5900), 351 (6500), 380 (470). *Anal.* Calcd for $C_{12}H_7Br$: C, 62.36; H, 3.05; Br, 34.58. Found: C, 62.36; H, 3.06; Br, 34.31.

Photochemical Synthesis of *endo*-7,10-Methano-6b,7,10,10a-tetrahydrofluoranthene (3a), *exo*-4a, and *exo*-Naphtho[1′,8′]tricyclo[3.3.0.0^{6,10}]deca-2,7-diene (5a). To a magnetically stirred mixture of 125 ml (1.45 mol) of freshly prepared cyclopentadiene and 410 ml of ethyl bromide contained in the reaction chamber of a Hanovia immersion apparatus submerged in an ice bath was added 1.0 g (0.003 mol) of recrystallized **1a**. The mixture was purged for 50 min with nitrogen and the purge maintained during the 16-min irradiation required for the yellow of **1a** to disappear. During the subsequent 6-hr interval an additional 9.0 g (0.03 mol) of **1a** was added at such a rate that its concentration never exceeded 1.25×10^{-2} *M*. The resulting reaction mixture was rotary evaporated to about 200 ml and filtered to remove some photodimer, and the filtrate was rotary evaporated to a yellow viscous oil. A portion of this oil was chromatographed on $AgNO_3$–silica gel following the method of Baker and Mason[10] to yield **3a** and **4a**; mass spectrum (70 eV) *m/e* (rel intensity): **3a**, 218 (3), 153 (18), 152 (100), 151 (8), 101 (3), 66 (16), 39 (7); **4a**, 218 (3), 153 (14), 152 (100), 151 (7), 101 (3), 66 (4), 63 (5), 39 (8).

To obtain **5a** the rest of the crude oil (10 g) was dissolved in 50 ml of absolute ether and a solution of 7.1 g (0.05 mol) of chlorosulfonyl isocyanate[47] in 20 ml of absoute ether was added dropwise to the ice-cooled mixture with continuous magnetic stirring. The mixture was allowed to come to room temperature and stirred at 25° for 16 hr. The mixture was poured onto crushed ice, vigorously stirred, washed successively with 2 × 50 ml of H_2O and 2 × 50 ml of saturated NaCl solution, and then dried over anhydrous Na_2SO_4. The resulting ether solution was passed over a 35 × 2.5 cm column of anhydrous Al_2O_3 packed in hexane. The first ether fractions to come off were rich in **5a** as determined by glc. These fractions were rotary evaporated to viscous yellow oils that were dissolved in hot methanol. Slow crystallization of the methanol solution deposited 0.5 g of white plates of **5a**, mp 89–90°. Final purification was achieved by vacuum sublimation at 0.05 mm and 70° to give pure white **5a**: mp 90–91°; ir (KBr) 3050, 2940, 2905, 2880, 2850 (CH), 1585 (C=C), 818, 775, 712, 664 cm^{-1}; nmr δ ($CDCl_3$) 2.6 (d, 2 H), 3.2 (s, 1 H), 3.8 (m, 2 H), 6.0 (m, 2 H), 7.4 ppm (m, 6 H); mass spectrum (70 eV) *m/e* (rel intensity) 218 (4), 202 (3), 153 (18), 152 (100), 151 (8), 150 (3), 101 (7), 66 (7), 63 (3), 39 (8). *Anal.* Calcd for $C_{17}H_{14}$: C, 93.54; H, 6.46. Found: C, 93.73; H, 6.45.

Photoproducts *endo*-7,10-Methano-6b,7,10,10a-tetrahydro-3-bromofluoranthene (3b), *exo*-4b, and *exo*-4′-Bromonaphtho[1′,8′]tricyclo[3.3.0.0^{6,10}]deca-2,7-diene (5b). A mixture of 120 ml of CH_2Br_2, 36 ml of cyclopentadiene, and 768 mg (0.0033 mol) of **1b** was equally divided among eight photolysis tubes, and each tube was purged with nitrogen and irradiated for 3 hr to give 95% disappearance of **1b** by glc. The combined photolysis mixtures were rotary evaporated and the viscous residue was taken up in about 2 ml of hexane. A portion of this mixture was subjected to preparative glc on a 2 ft × 0.25 in. 10% OV-17 column at 194°. Isomers **3b** and **4b** were collected in one fraction to yield a viscous pale yellow oil: nmr δ (CCl_4) 0.8 (s), 1.0 (s,) 1.2 (m), 1.4 (m), 1.7 (m), 2.8 (s), 3.2 (m), 3.5 (s), 4.0 (s), 5.3 (m, vinyl), 6.3 (m, vinyl), 7.0–7.8 ppm (m, aromatic); ir (film) 3050, 2960, 2875, 2860, 1610, 1600, 828, 775, 730, 685 cm^{-1}; mass spectrum (70 eV) *m/e* (rel intensity): **3b**, 298 (3), 296 (3), 233 (12), 232 (91), 231 (14), 230 (100), 188 (5), 163 (7), 153 (3), 152 (13), 151 (78), 150 (25), 75 (12), 66 (10); **4b**, 298 (3), 296 (3), 233 (12), 232 (96), 231 (14), 230 (100), 215 (4), 189 (4), 152 (12), 151 (71), 150 (24), 101 (7), 66 (11), 39 (9). *Anal.* Calcd for $C_{17}H_{13}Br$: C, 68.70; H, 4.41; Br, 26.89. Found: C, 68.80; H, 4.29; Br, 26.69.

The remaining portion of the hexane mixture was chromatographed on a $AgNO_3$–silica gel column according to the procedure described by Baker and Mason.[10] The first fractions to come off with ligroin were rich in isomer **5b**. These fractions were rotary evaporated and the viscous residue was taken up in hot methanol, treated with charcoal, filtered, and crystallized to yield 75 mg of colorless crystals, mp 96–99°. Sublimation (70° (0.05 mm)) yielded 17 mg of pure **5b**: mp 96–98°; nmr δ (CCl_4) 2.70 (m, 2 H), 3.18 (m, 1 H), 3.80 (m, 2 H), 5.95 (m, 2 H, vinyl), and 7.0–8.0 ppm (m, 5 H, aromatic); ir (KBr) 3025, 2940, 2900, 2845, 1600, 1075, 828, 775, 735 cm^{-1}; mass spectrum (70 eV) *m/e* (rel intensity) 298 (4), 296 (4), 233 (13), 232 (90), 231 (14), 230 (100), 215 (8), 153 (3), 152 (16), 151 (76), 150 (24), 108 (8), 101 (9), 75 (10), 66 (14), 39 (13). *Anal.* Calcd for $C_{17}H_{13}Br$: C, 68.70; H, 4.41; Br, 26.89. Found: C, 68.76; H, 4.50; Br, 26.89.

Thermal Diels–Alder Reaction between 1b and 2. A mixture of 750 mg (0.00325 mol) of **1b**, 15.0 ml of cyclopentadiene, and 15.0 ml of benzene was sealed in a Griffen–Worden pressure tube and heated to 120° for 17 hr. Glc analysis of the mixture on column A

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indicated two products with retention times identical with those of **3b** and **4b** in a ratio of 4:1 respectively. The mixture was concentrated by vacuum distillation with removal of all volatile material with a boiling point less than 60° (3 mm). The residual viscous oil was treated with an equal volume of hexane, filtered from precipitated polymer, and chromatographed on $AgNO_3$–silica gel.[10] The combined fractions rich in **3b** and **4b** were rotary evaporated and collected after passage through the preparative glc using a 1 ft × 0.25 in. 10% OV-17 column at 194°. The viscous yellow oil (42 mg) was dissolved in 200 μl of hot hexane and allowed to crystallize, and the collected crystals were subjected to sublimation at 65° (0.05 mm). The off-white solid had a melting point of 79–82°. A nmr spectrum of this solid (CCl_4) showed the same resonances as the mixtures obtained from the photolysis runs. However, the amount of **4b** remaining in the solid was estimated to be about 5% after the extensive purification.

Thermal Isomerization of 5b to 3b. A sample of **5b** injected into the glc with column B maintained above 170° produced a new peak with retention time identical with that of **3b**. At column temperatures above 225° isomerization of **5b** to **3b** is complete. A mixture of 5 mg of **5b** and 5 ml of undecane (bp 192–194°) when refluxed for 15 hr achieved a 65% isomerization of **5b**. Repeated injections of **5b** onto column B maintained at 228° followed by collection of the effluent yielded 2.6 mg of a compound whose nmr spectrum proved identical with that of **3b**.

Bis(dicyclohexyl-18-crown-6-ether) Complex of Disodium Bengal Red. Bengal Red (Aldrich), 1.0 g (1.0 mmol) in 30 ml of H_2O, was treated with 1.5 ml (9 mmol) of 6 *N* HCl and extracted with three 30-ml portions of methylene chloride, then two 30-ml portions of ether. The combined extracts were washed with 50 ml of H_2O, dried over $MgSO_4$, filtered, and rotary evaporated to yield 730 mg (0.75 mmol) of neutralized Bengal Red. This was dissolved in 50 ml of methanol and filtered, and sodium methoxide (from 1.60 mmol of sodium metal) in 10 ml of methanol added, giving a deep red solution. Dicyclohexyl-18-crown-6-ether (Aldrich, technical), 564 mg (1.48 mmol) in 10 ml of methanol, was added and the solution rotary evaporated 2 hr at 40° to give 1.28 g of dark red mass. This was taken up in 75 ml of methylene chloride, filtered, and added dropwise to 150 ml of stirred ligroin (bp 63–75°), and the resulting precipitate was filtered to yield 300 mg of fine red solid. The filtrate was rotary evaporated, dissolved in 40 ml of methylene chloride, and treated with ligroin to yield a second crop of 784 mg, for a total of 1.084 g (0.62 mmol, 62%). The ir spectrum (KBr) is identical with that of Bengal Red[48] plus absorptions due to the starting dicyclohexyl-18-crown-6-ether. The visible spectrum is similar to that of Bengal Red,[49] having λ_{max} in methylene bromide of 569 nm (ϵ 41,000). *Anal.* Calcd for $C_{60}H_{74}Cl_4I_4O_9Na_2$: C, 40.88; H, 4.23; I, 28.80; Na, 2.61. Found: C, 39.98; H, 4.98; I, 25.34; Na, 2.54.

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[48] Sadtler Standard Infrared Spectrum No. 1573, Philadelphia, Pa.

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Assessment of the Relative Efficiencies of Syn-Disposed Cyclopropane, Cyclobutane, and Cyclobutene Ring Participation in the Photolysis of Azo Compounds. Kinetic Analysis of a *cis*-Bicyclo[5.2.0]nona-2,5,8-triene to *cis*-Bicyclo[6.1.0]nona-2,4,6-triene Rearrangement

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Abstract: The *cis*-bicyclo[5.2.0]nona-2,5,8-triene (**15**) has been synthesized and its thermal (−6 to −25°) rearrangement to the isomeric *cis*-bicyclo[6.1.0]nona-2,4,6-triene (**16**) examined kinetically. The activation parameters, $\Delta H^{\ddagger} = 13.6$ kcal/mol, $\Delta G^{\ddagger} = 19.7$ kcal/mol, and $\Delta S^{\ddagger} = -20.4$ eu, follow directly from the experimentally derived rate constants. The structurally related *cis*-bicyclo[5.2.0]nona-2,5-diene (**22**) was similarly prepared; in contrast to **15**, **22** exhibits no tendency to undergo Cope rearrangement. Access to **15** and **22** was gained by extrusion of nitrogen from azo compounds **14** and **21**. Low-temperature photolysis studies and selected thermal experiments have established that the fused cyclopropane bond in these tetracyclic molecules experiences rupture to the exclusion of similar bonds of the cyclobutene and cyclobutane type. These data lead to the conclusion that strained rings experience cleavage in radical reactions chiefly as a function of their "bent bond" character. In contrast, the direction of equilibria in the [3,3]sigmatropic rearrangement processes is dictated by strain factors.

The capability of three- and four-membered carbocyclic rings to function effectively as neighboring groups when fused in close proximity to developing bridged cationic centers has been recently examined. Not only has the necessity for endo stereochemical orientation of the small ring been convincingly demonstrated, but a parallelism between chemical reactivity and ring size has been noted. For example, whereas the solvolytic rate constant for **1** is merely comparable to that of the 7-norbornyl derivative, tosylate **2** exhibits a 10^{14}-fold rate acceleration.[1] Also, although the cyclobutene ring in **4** is unable to participate in the ionization process,[2] **5** enjoys a relative rate of $10^{5.8}$.[3] Anchimeric assistance by the cyclobutane

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[2] R. M. Coates and K. Yano, *ibid.*, **95**, 2203 (1973).

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