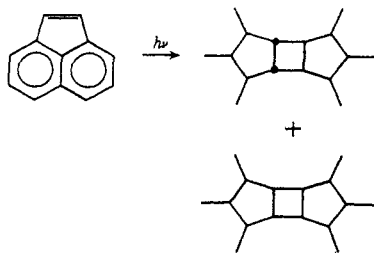


The Photodimerization of Acenaphthylene. Mechanistic Studies<sup>1</sup>Dwaine O. Cowan<sup>2</sup> and Ronald L. E. Drisko<sup>3</sup>*Contribution from the Department of Chemistry, The Johns Hopkins University, Baltimore, Maryland 21218. Received March 12, 1970*

**Abstract:** Acenaphthylene dimerizes under direct or sensitized photolysis conditions to form cis and trans dimers. The relative quantum yield of dimerization as well as the ratio of dimers (cis/trans) is shown to depend linearly on the acenaphthylene concentration, over the concentration range studied. The cis-dimer formation is dominant in polar solvents and in the irradiation of concentrated solutions of acenaphthylene. Heavy atom solvents in small amounts of mixed solvents increase the amount of trans dimer and reduce the amount of cis dimer formed. Ferrocene and oxygen quench the (triplet) precursor of the trans dimer but only slightly reduce the cis-dimer formation. Sensitized dimerization studies were used to bracket the energy of the spectroscopically undetected triplet state of acenaphthylene (43–45 kcal/mol). All of the data presented are consistent with a mechanism involving two reactive species, a singlet excimer and an acenaphthylene triplet. The singlet excimer forms only cis dimer (>98%) and the triplet state reacts to form both trans and cis dimers (the ratio depending upon solvent polarity). For example, in cyclohexane containing 10 mol % ethyl iodide the triplet species reacts to form 80% trans and 20% cis dimer.

Over fifty years ago the effect of light on acenaphthylene was observed and reported in a series of papers by Dziewonski and coworkers.<sup>4a-c</sup> It was found that, upon exposure to sunlight, acenaphthylene forms two distinct dimers whose ratio varies with acenaphthylene concentration and with solvent, the lower melting isomer (designated as  $\beta$ -heptacyclene) being predominant in high concentrations or in ligroin. This photodimerization was investigated in a more quantitative manner in 1947 by Bowen and Marsh<sup>5</sup> who determined the quantum yields for the disappearance of acenaphthylene as a function of concentration and of solvent. Two mechanisms were proposed to account for the data obtained; that favored by the authors involved the participation of van der Waals  $\pi$  complexes.

The structures of the dimers, assigned by Dziewonski as stereoisomeric cyclobutanes,<sup>4b</sup> was confirmed by Dunitz and Weisman<sup>6</sup> through X-ray analysis of the purified products. The high melting isomer was thus determined to be the trans dimer. The cis structure of the low-melting isomer was shown by Griffin and Veber<sup>7</sup> through ozonolysis, oxidative decomposition, and esterification to obtain a product identified as *cis,cis,cis*-1,2,3,4-tetracarboxymethoxycyclobutane. More



recent studies<sup>8-10</sup> on the photodimerization of

(1) Photochemical Reactions. IV. Part III: D. O. Cowan and A. Baum, submitted for publication.

(2) A. P. Sloan Fellow; to whom correspondence should be addressed.

(3) du Pont Postgraduate Teaching Fellow, 1965–1967.

(4) (a) K. Dziewonski and G. Rapalski, *Chem. Ber.*, **45**, 2491 (1912);

(b) K. Dziewonski and C. Paschalski, *ibid.*, **46**, 1986 (1913); (c) K. Dziewonski and Z. Leyko, *ibid.*, **47**, 1679 (1914).

(5) E. J. Bowen and J. D. F. Marsh, *J. Chem. Soc.*, 109 (1947).

(6) J. D. Dunitz and L. Weisman, *Acta Crystallogr.*, **2**, 62 (1949).

(7) G. W. Griffin and D. F. Veber, *J. Amer. Chem. Soc.*, **82**, 6467 (1960).

(8) R. Livingston and K. S. Wei, *J. Phys. Chem.*, **71**, 541 (1967).

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

acenaphthylene indicate that the mechanism of this reaction is considerably more complex than proposed by Bowen and Marsh. In a preliminary communication,<sup>10</sup> we presented solvent effect data bearing on selected mechanistic details of the reaction. We now describe these results in full and report further findings: concentration effect on isomer ratio, quenching studies, and sensitized reactions, allowing a more complete understanding of the reaction mechanism.

## Results

**Solvent and Concentration Effects.** Tables I and II show the effect of acenaphthylene concentration on

**Table I.** The Photodimerization of Acenaphthylene in Cyclohexane

Acenaphthylene, <sup>a</sup> g	Dimer yield, g	$\phi_{rel}^b$	cis, g	trans, g	% cis	% trans	cis/ trans
5.0	2.72	1.00	2.14	0.58	78.7	21.3	3.69
10.0	4.77	1.75	3.86	0.91	80.9	19.1	4.24
15.2	6.51	2.39	5.42	1.09	83.2	16.8	4.97
30.0	10.80	3.89	9.38	1.42	86.8	13.2	6.60

<sup>a</sup> Grams of acenaphthylene/150 ml of cyclohexane. <sup>b</sup> Relative to dimer yield in the irradiation of 5 g of acenaphthylene in 150 ml of cyclohexane. Under these conditions, light absorption is completed over the entire concentration range studied; *i.e.*, the optical density is greater than 2, at the primary wavelength of photolysis (3650 Å).

**Table II.** The Photodimerization of Acenaphthylene in Benzene or Methanol

Acenaphthylene, <sup>a</sup> g	Dimer yield, g	$\Phi_{rel}^b$	cis, g	trans, g	% cis	% trans	cis/ trans
5.0 <sup>c</sup>	3.72	1.37	2.36	1.36	63.4	36.6	1.74
10.0	7.18	2.64	4.89	2.29	68.1	31.9	2.14
15.2 <sup>c</sup>	9.62	3.54	6.80	2.82	70.6	29.4	2.41
30.0 <sup>c</sup>	16.10	5.92	11.89	4.21	73.9	26.1	2.81
15.2 <sup>d</sup>	6.27	2.31	5.34	0.93	85.2	14.8	5.74

<sup>a</sup> Grams of acenaphthylene/150 ml of solvents. <sup>b</sup> Relative to dimer yield in the irradiation of 5 g of acenaphthylene in 150 ml of cyclohexane (see Table I). <sup>c</sup> In benzene. <sup>d</sup> In methanol.

(10) (a) D. O. Cowan and R. L. Drisko, *Tetrahedron Lett.*, 1255 (1967); (b) D. O. Cowan and R. L. Drisko, *J. Amer. Chem. Soc.*, **89**, 3069 (1967).

the dimer yield in cyclohexane, methanol, and benzene solutions. Unless specifically noted all irradiations were carried out as previously reported for a period of 15 hr under continuous purging with purified nitrogen. The data show that the cis dimer predominates in both cyclohexane and benzene solutions, although more strongly in the former. It is seen that as the acenaphthylene concentration is increased, proportionally more cis is formed. This effect is slightly more pronounced in cyclohexane than in benzene. Increases in the yield of dimer with increasing concentration would of course be expected as the dimerization is a bimolecular process. However, if both dimers were formed in a similar fashion, the concentration dependence should be the same for each isomer. The yields of dimer in these three solvents increase as methanol < cyclohexane < benzene. It is seen that the yields of the cis dimer also increase in this manner, although the percentage of cis product increases in the inverse order. The trans yield is also seen to be solvent dependent and varies from methanol to benzene in the same manner as the cis although to a different degree.

**Quenching Experiments.** In order to determine the multiplicity of the reactive species, the photodimerization was carried out in the presence of various triplet quenchers. The results of attempts to quench the dimerization with tris(acetylacetonato)iron(III) (ferric acetylacetonate) are given in Table III. Comparison

**Table III.** The Photodimerization of Acenaphthylene in the Presence of Quenchers<sup>a</sup>

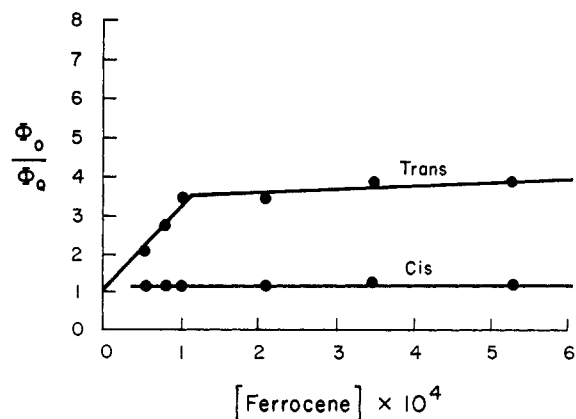
Quencher, <i>M</i>	Dimer yield, g	% reac- tion	cis, g	trans, g	% cis	% trans	cis/ trans
$1 \times 10^{-4}$ <sup>b,e</sup>	6.48	42.7	5.01	1.47	77.3	22.7	3.41
$1 \times 10^{-3}$ <sup>b,c,e</sup>	6.36	41.9	5.30	1.06	83.3	16.7	5.00
$1 \times 10^{-4}$ <sup>d,e</sup>	8.94	58.8	6.42	2.52	71.8	28.2	2.55
<i>d</i>	9.62	63.2	6.80	2.82	70.6	29.4	2.41
O <sub>2</sub> (sat) <sup>d</sup>	5.95	39.1	5.84	0.11	98.2	1.8	53.1

<sup>a</sup> All determinations on 15 g of acenaphthylene/150 ml of solvent for 15.0 hr. <sup>b</sup> Cyclohexane as solvent. <sup>c</sup> Irradiated for 18.5 hr to compensate for filter effect. <sup>d</sup> Benzene as solvent. <sup>e</sup> Ferric acetylacetonate.

of the results listed in Table III with those in Table II indicates that ferric acetylacetonate has little quenching effect. The slight decreases in dimer yield for the irradiations containing  $1 \times 10^{-4}$  *M* chelate can be attributed to some absorption (*ca* 5%) of the light by the chelate. In addition the discrepancies between the yields of cis and trans dimer in these photolyses and those without chelate are attributed to inaccuracy in the spectrophotometric determination of the dimers, caused by the trace amounts of ferric acetylacetonate in the product crystals.

The results of oxygen quenching in benzene are also given in Table III. It is obvious that the presence of oxygen exerts a large quenching effect on the production of the trans dimer and a smaller but significant effect on the formation of the cis dimer. In fact, the formation of the trans dimer is decreased by oxygen by a factor of 25 while the cis dimer is decreased by a factor of 1.2.

The third triplet quencher investigated was ferrocene ( $E_t < 43$  kcal/mol). These results are presented in



**Figure 1.** Stern-Volmer plot of the quenching of acenaphthylene cis- and trans-dimer formation by ferrocene.

Table IV. As with oxygen, the production of the trans dimer was quenched in the presence of ferrocene. A plot of  $\Phi_0/\Phi_Q$  vs. the molar concentration of ferrocene (Stern-Volmer plot) is presented in Figure 1 for both cis and trans dimers.  $\Phi_0$  is the dimer yield in the absence of quencher. It is seen that for trans, quenching is linear for concentrations up to about  $1 \times 10^{-4}$  *M* ferrocene, whereupon a marked change in slope occurs and the quenching continues slowly but still in a linear manner. The cis dimer, however, is quenched only slightly and quenching is not increased as the concentration of ferrocene is increased.

**Table IV.** The Quenching of Acenaphthylene Photodimerization with Ferrocene

Ferrocene, <sup>a</sup> <i>M</i>	Dimer yield, g	% reac- tion	cis, g	trans, g	% cis	% trans	cis/ trans
$5.67 \times 10^{-5}$	5.09	33.5	4.55	0.54	89.4	10.6	8.43
$8.03 \times 10^{-5}$	5.09	33.5	4.68	0.41	91.9	8.1	11.41
$1.06 \times 10^{-4}$	5.22	34.3	4.90	0.32	93.9	6.1	15.31
$2.10 \times 10^{-4}$	4.87	32.0	4.55	0.32	93.4	6.6	14.22
$3.49 \times 10^{-4}$	4.78	31.4	4.50	0.28	94.1	5.9	16.07
$5.31 \times 10^{-4}$	4.87	32.0	4.59	0.28	94.2	5.8	16.40
0.00	6.51	42.9	5.42	1.09	83.2	16.8	6.60

<sup>a</sup> 15.2 g of acenaphthylene/150 ml of cyclohexane irradiated for 15.0 hr.

**The Photosensitized Dimerization.** Table V shows that the dimerization of acenaphthylene can be sensitized by molecules of triplet energy  $\geq 44.6$  kcal/mol. The maximum yields of dimer for crystal violet and hematoporphyrin are 0.07 and 0.15 g, respectively. These limits arise from uncertainties in the experimental work-up, as no product could be visually detected. It should be noted that the relative dimer yields cannot be related as no attempt was made to ensure equal irradiation periods or that equal quantities of light were absorbed. It appears therefore that the lowest triplet state of acenaphthylene must lie between 39 and 44.6 kcal/mol. Since there are few suitable sensitizers of triplet energy in this region, no more precise determination was attempted. It is noted, however, that ferrocene ( $E_t < 43$  kcal/mol) served to quench the formation of the trans dimer. Thus, the triplet energy of acenaphthylene must be equal to or higher than that of ferrocene.

Table V. The Sensitized Dimerization of Acenaphthylene<sup>a</sup>

Sensitizer	$E_T$ , kcal/mol	Dimer isolated, g	cis, g	trans, g	% cis	% trans	cis/trans
Eosin-y	46.8 <sup>a</sup>	1.54	0.47	1.07	30.5	69.5	0.44
Rose bengal	44.6 <sup>a</sup>	2.77	1.02	1.75	36.8	63.2	0.58
		5.25	1.82	3.43	34.7	65.3	0.53
Crystal violet	39	<0.07					
Hematoporphyrin	37.2 <sup>a</sup>	<0.15					
Methylene blue	33.5 <sup>a</sup>	0.00					

<sup>a</sup> Acenaphthylene (11.5 g) in 115 ml of methanol solution of sensitizer with constant nitrogen purging.

### Discussion and Conclusions

It has been seen that the photodimerization of acenaphthylene is significantly concentration and solvent dependent. These dependences are shown in Tables I and II and in Figure 2. In addition Figure 3 shows

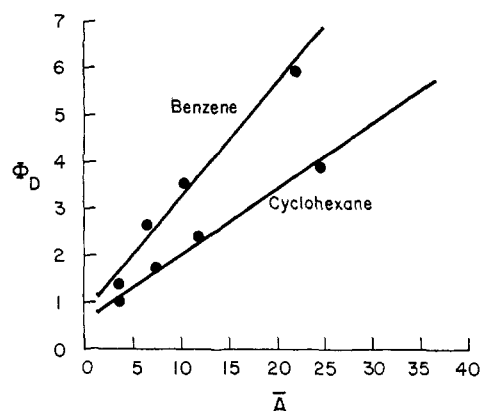
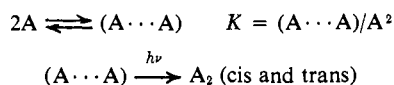


Figure 2. Relative quantum yields of photodimerization of acenaphthylene in benzene and cyclohexane as a function of the acenaphthylene concentration.

that the dimer ratio (cis/trans) is linearly dependent on the acenaphthylene concentration in both benzene and cyclohexane. Bowen and Marsh have proposed that an associated species,  $\pi$  complex, is an intermediate in both the formation of the cis and trans dimers.



Since it is difficult to conceive of how a  $\pi$  complex could (a) lead to large yields of trans dimer (as would be necessary if both dimers were produced from such a species), (b) exhibit a concentration effect greater for cis than trans, and (c) have a solvent effect in which the yield of cis varies by a factor of  $\sim 1.3$  from methanol to benzene while the yield of trans varies by a factor of  $\sim 3$ , it must be concluded that the two dimers are produced by two (or more) distinct excited species.

The quenching of the trans dimer with oxygen and ferrocene indicates that this product is formed almost entirely from the triplet state. It is possible to calculate the amount of triplet-derived product in benzene by subtracting the amount of product obtained in the presence of oxygen from the amount of product obtained in the absence of oxygen. Such a calculation indicates that acenaphthylene triplets in benzene give both trans and cis dimers in the ratio of 74:26. The triplet state accounts for almost all of the trans product and about

10% of the cis product. Since in the experiments using ferrocene as quencher, the production of the cis dimer does not appear to be dependent upon the ferrocene concentration (at least in the concentration range studied) the small amount of quenching of cis observed may arise from quenching of the same state responsible for the production of the trans dimer. A break in the slope of the Stern-Volmer plot for the trans dimer may

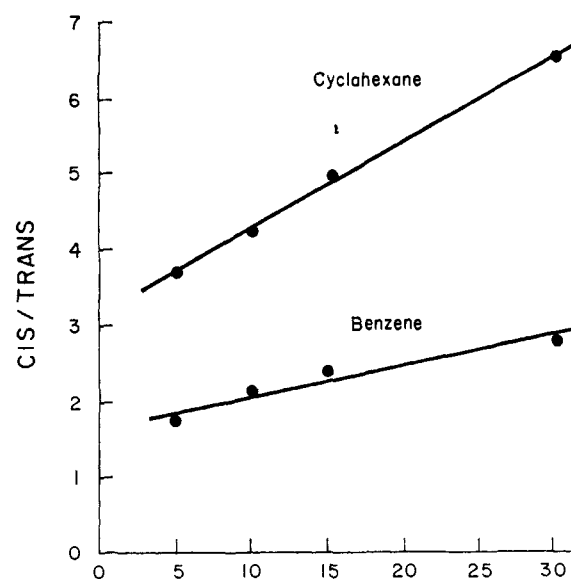


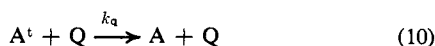
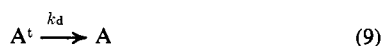
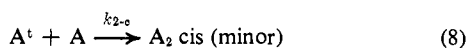
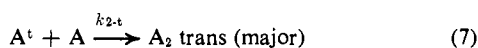
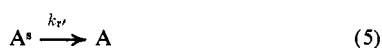
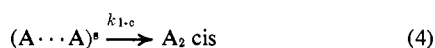
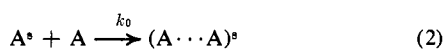
Figure 3. Ratio of *cis*- to *trans*-acenaphthylene dimers formed in benzene and cyclohexane as function of acenaphthylene concentration.

be attributed to the presence of two excited species which are quenched at different rates. These two species could be (a) two different monomeric acenaphthylene triplet states  $T_1$  and  $T_2$  or (b) a monomeric acenaphthylene triplet state  $T_1$  and a triplet excimer. This second triplet species is of relatively minor importance in the overall reaction since less than 5% of the total product in an unquenched reaction is due to this species (0.3 g/6.5 g).

Comparison of the dimer distribution from the direct photolysis of acenaphthylene (0.67 *M*) in methanol to that for the same concentration in the presence of a sensitizer indicates that the predominance of cis observed in the direct photolysis is reversed in the photosensitized process. Assuming that the presence of the sensitizer exerts no effect other than energy transfer, one would expect the dimer ratios to be identical in both cases if all products were triplet derived. It appears again that one of the products, the cis dimer,

must be formed from *two states of different multiplicity*. Since the cis dimer is only slightly quenched by oxygen or ferrocene a singlet reaction is indicated for this species. Since trans is almost totally eliminated by quenching it appears that the singlet reaction forms only the cis dimer. Inasmuch as the singlet species exclusively forms the cis dimer it is reasonable to propose that this singlet species is either formed from a ground-state  $\pi$  complex or is a singlet excimer. The general conclusion that acenaphthylene singlets are only indirectly involved is also consistent with solvent effect and rate data to be discussed later in this paper.

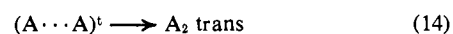
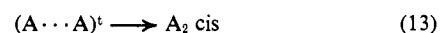
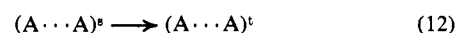
The magnitude of the cis/trans isomer ratio decreases from methanol to cyclohexane to benzene. The solubility of acenaphthylene also *increases* in this order. It appears therefore that the solvent effect may arise from a greater amount of self-association ( $A \cdots A$ ) in poorer solvents. However, just the converse can be argued since the absolute amount of cis dimer increases in going from methanol to benzene. It is noted that the yield of trans dimer also is increased in proceeding from methanol to cyclohexane to benzene. The variation in dimer yields in these three solvents requires an explanation in addition to the simple postulation of cis-forming  $\pi$  complexes. In addition a systematic investigation of the ultraviolet spectrum of acenaphthylene over a wide range of concentrations failed to reveal any evidence of absorption due to aggregates, nor was any definite evidence found in a recent study by Livingston and Wei.<sup>11</sup> We therefore propose the following mechanism where the acenaphthylene triplet state forms both cis and trans dimers and the acenaphthylene singlet excimer forms only the cis dimer. The symbols A,



( $A \cdots A$ )<sup>s</sup>, and  $A_2$  refer to acenaphthylene monomer, its singlet excimer, and its stable dimer either cis or trans.  $I_a$  is the rate of light absorption while  $k_{1-c}$ ,  $k_{2-c}$ , and  $k_{2-t}$  refer to the rate constants for product formation (cis or trans),  $k_r$ ,  $k_{r'}$ , and  $k_d$  refer to rate constants for nonradiative transitions to the ground state,  $k_{isc}$  is the rate constant for intersystem crossing from the singlet to the triplet state,  $k_q$  and  $k_{a'}$  are rate constants for quenching, and  $k_0$  is the rate constant for excimer for-

(11) Livingston and Wei<sup>8</sup> have reported an apparent molecular weight of 154 slightly higher than that required for  $C_{12}H_8$  (152).

mation. Other reactions, such as the formation (eq 12) and reaction (eq 13–15) of an unquenchable triplet ex-



cimer, could be added but are not required to account for the data. It is quite reasonable that the excimer should exclusively form the cis dimer because of the geometrical requirements (maximum charge transfer and exciton interaction) for excimer formation. Because both exciton and charge-transfer interactions can be important in the excimer bonding it is difficult to predict the exact effect of solvent polarity. Birks has shown that there is no solvent effect when only exciton interactions are important while a number of others have observed a solvent effect on systems where presumably charge-transfer interactions are important.<sup>12</sup>

Reactions 3 and 5 have been included to account for the low quantum yields of this dimerization.<sup>5,8,13</sup> Since acenaphthylene is nonfluorescent<sup>14</sup> and the yields of cis dimer indicate that the major portion of the product is formed from the singlet manifold, nonradiative decay from the lowest singlet state must be an important process in the acenaphthylene molecule.

A further indication of the importance of internal conversion is found in heavy atom solvent experiments to be considered in detail in another paper. We should point out here that qualitatively the heavy atom solvents dramatically increase the formation of the trans dimer and decrease but do not eliminate the formation of the cis dimer. For example, a change from pure cyclohexane to cyclohexane containing 10 mol % ethyl iodide increases by a factor of 2, the total conversion, produces a tenfold increase in the amount of trans dimer formed, and reduces the amount of cis dimer by a factor of about 2. These general results are consistent with the heavy atom solvent increasing the probability of intersystem crossing (eq 6) with the result that more trans product is formed (eq 7) and less cis product is formed (eq 2, 4). The total yield is increased because of the relative importance of internal conversion from the singlet state (eq 3, 5).

After the appearance of our preliminary communications a report appeared by Hartmann, Hartmann, and Schenck.<sup>9</sup> This work is in general agreement with our conclusions and contained one very interesting correlation. The influence of a number of solvents was described with the use of Kirkwood–Onsager solvent parameters, using the method formulated by Berson, Hamlet, and Mueller<sup>15</sup> (an empirical method for the correlation of reaction rate with the ability of the sol-

(12) A. Dammers-de-Klerk, *Mol. Phys.*, **1**, 141 (1958); J. Ferguson, *J. Chem. Phys.*, **28**, 765 (1958); F. Smith, A. Armstrong, and S. McGlynn, *ibid.*, **44**, (1966); H. Morrison, H. Curtis, and T. McDowell, *J. Amer. Chem. Soc.*, **88**, 5415 (1966); R. L. Barnes and J. B. Birks, *Proc. Roy. Soc., Ser. A*, **291**, 570 (1966).

(13) The absolute quantum yield for dimer formation when the acenaphthylene concentration is 0.67 M is 0.034 (3650-Å light). This value is in reasonable agreement with those given by Bowen and Marsh,<sup>5</sup> and also Livingston and Wei.<sup>8</sup>

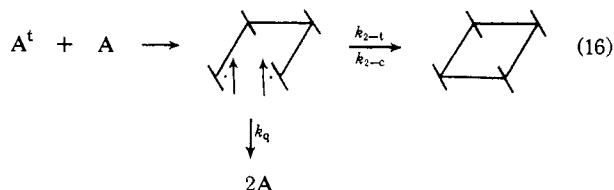
(14) A weak fluorescence has been reported<sup>8</sup> but may have resulted from a persistent impurity.

(15) J. A. Berson, Z. Hamlet, and W. A. Mueller, *J. Amer. Chem. Soc.*, **84**, 297 (1962).

vent to stabilize the change in dipole moment in proceeding to the transition state). A linear plot of  $\log(\text{trans/cis})$  vs. the expression  $(D - 1/2D + 1)P/M$ , where  $D$  is dielectric constant,  $P$  is the density, and  $M$  is the molecular weight of the solvent, was obtained for the product ratios of the Rose Bengal photosensitized reaction. This indicates that the solvent effect in the photosensitized case is the result of increased stabilization of the transition state leading to the cis dimer (dipoles parallel) relative to that leading to the trans (dipoles opposed) as the polarity of the solvent is increased.

In addition it was found that the dimerization can be partially quenched by cyclooctatetraene ( $E_t \approx 39$  kcal/mol), which, at least within the accuracy of the gravimetric analysis used by these workers, completely eliminated the formation of the trans dimer. It was noted that the ratio of the dimers formed from the quenched state (calculated from the results in the absence of quencher and those in the presence of quencher) as a function of solvent showed the same correlation with the Kirkwood-Onsager solvent parameters as the ratio of the photosensitized adducts, indicating that the quenched and photosensitized states are identical (within the limits set by their analytical results).

We would like to point out that, since Schenck found no heavy atom effect on the sensitized or quenched reaction (sensitized dimerizations in heavy atom solvents followed the Kirkwood-Onsager relationship), the heavy atom effect we have observed on the direct photolysis cannot be interpreted as an increased efficiency of triplet dimerization,  $k_{2-t}$  and  $k_{2-c}$  (reaction 16), but only as an increased efficiency of intersystem crossing,  $k_{isc}$  (eq 6).



In addition by combining Schenck's data with ours it is possible to present another argument in favor of the excimer mechanism. Schenck has shown that the triplet component of the dimerization in nonpolar solvents gives rise to 80–85% trans and 20–25% cis dimer. Our data indicate that cyclohexane containing 10 mol % ethyl iodide gives about 80% trans and 20% cis dimer. This is exactly what we would predict, from Schenck's data, for a reaction entirely from the triplet state. This indicates that most if not all of the singlet species are undergoing intersystem crossing to the triplet state and are not forming singlet excimers with ground-state acenaphthylene molecules.

If ground-state  $\pi$  complexes were competing for light, the product should be derived from both the excited  $\pi$  complexes and the triplet states giving more cis dimer than predicted from Schenck's data.

Assuming the usual steady-state approximations for the reaction scheme given, the following expression can be derived for the total quantum yield of dimerization

$$\Phi_{A_2} = K_1[A] + K_2 \quad (17)$$

when  $k_0[A] \gg k_{r'} + k_{isc}$  and when  $(k_{q'} + k_{2-c} +$

$k_{2-t})[A] \gg k_q[Q] + k_d$ , where  $K_1$  and  $K_2$  are rate ratios.<sup>16</sup> The first simplification is probably reasonable since we know that the quantum yields are very low<sup>13</sup> ( $k_{r'}$  large) and the second is reasonable for nitrogen-flushed solutions ( $k_q[Q]$  small).

Equation 17 predicts that the quantum yield should increase linearly with the acenaphthylene concentration. Figure 2 shows that this is true for the concentration range used in this study. It appears, therefore, that this mechanism is consistent with the kinetic data insofar as the above assumptions and approximations are valid. From the expressions for the rate of production of the cis and trans dimers for this mechanism it is possible to show<sup>16</sup> that the expression for the ratio of these isomers has the following form. Figure

$$\frac{[\text{cis}]}{[\text{trans}]} = \frac{K_4}{K_5} + \frac{K_3}{K_5}[A]$$

3 indicates that the cis/trans ratio does increase linearly with the acenaphthylene concentration.<sup>17</sup>

## Summary

The proposed mechanism is consistent with all of the kinetic and spectroscopic data we have presented. (a) The relative  $\Phi$  for dimer formation is a linear function of acenaphthylene concentration  $[A]$  over the concentration range studied. (b) The ratio of cis/trans dimers formed is a linear function of acenaphthylene concentration. (c) Heavy atom solvents (even in low concentrations) increase the amount of trans dimer and reduce the amount of cis dimer formed. (d) Polar solvents favor the formation of the cis dimer (via an excimer). (e) Ferrocene and  $O_2$  quench the triplet precursor of the trans dimer but only slightly reduce the cis dimer formation. (f) No spectroscopic evidence could be found for ground-state complexes. (g) Sensitized dimerization studies bracketed the triplet energy of acenaphthylene (43–45 kcal/mol). However, the triplet state of acenaphthylene could not be spectroscopically observed by Livingston or in this study. From the sensitized reactions the triplet acenaphthylene (in methanol) gives about 70% trans dimer and 30% cis dimer. From the oxygen-quenching experiments (benzene) it is possible to calculate by difference the percentage of cis and trans dimers due to acenaphthylene triplets in the unquenched experiment: 75% trans and 26% cis. If it is assumed that all of the dimerization in 10% ethyl iodide in cyclohexane is from the triplet state then the acenaphthylene triplet in this solvent reacts to form 80% trans and 20% cis dimers. While the acenaphthylene triplet gives both cis and trans dimers (the ratio depending on solvent polarity) the unquenchable state (excimer) gives almost all cis dimer (>98% calculated on the basis of the oxygen quenching experiment).

(16) R. L. Drisko, Ph.D. Dissertation, The Johns Hopkins University, Baltimore, Md., 1968.

(17) NOTE ADDED IN PROOF. Chu and Kearns have recently shown that the cis but not the trans dimer in EPA (300–195°K) gives a broad fluorescence emission due to a singlet excimer. This excited state was also demonstrated to lead to dimer dissociation. No evidence for a triplet excimer was found: N. Y. C. Chu and D. R. Kearns, *J. Phys. Chem.*, **74**, 1255 (1970).

## Experimental Section

**General.** It was observed that the purity of commercially available acenaphthylene varied vastly. The acenaphthylene used for most of the study was supplied by K and L Laboratories (mp 86.5–89.5°). This material was normally recrystallized and vacuum sublimed before use (mp 90–91°).

Product mixtures rich in the cis and trans dimers of acenaphthylene were prepared by irradiation in cyclohexane and benzene, respectively. In each case the insoluble dimers were separated from the starting material by repeated extraction of acenaphthylene from the product residues with cyclohexane. The products were then further purified by fractional crystallization. Product mixtures rich in the cis isomer (those precipitated from cyclohexane) were partially dissolved in hot cyclohexane. The insoluble residue (mainly the trans dimer) was filtered off and the filtrate allowed to cool. Repeated recrystallizations of the material thus obtained yielded splendidly formed white prisms (mp 231–233.5°). Pure trans dimer was isolated as fine white needles from benzene, mp 305–307°, by repeated recrystallization of product mixtures precipitated from irradiated benzene solution.

All ultraviolet spectra were recorded on a Cary Recording spectrophotometer, Model 14R. Solutions of pure cis and pure trans isomers in cyclohexane were prepared and the molar absorptivities determined. Fisher Certified cyclohexane was found to be suitable for analysis at the wavelengths of interest. The molar absorptivities determined were: cis,  $\epsilon_{219} = 1.27 \times 10^5$  l./mol cm,  $\epsilon_{225} = 6.60 \times 10^4$  l./mol cm; trans,  $\epsilon_{219} = 7.38 \times 10^4$  l./mol cm,  $\epsilon_{225} = 1.19 \times 10^5$  l./mol cm.

The composition of the product dimer mixtures was determined by measuring the optical densities of cyclohexane solutions of these dimers at 219 and 225 m $\mu$ . The concentrations of cis and trans dimer could therefore be calculated from these optical densities and absorptivities of the purified isomers.

To determine the accuracy to be expected from this analytical procedure, a solution containing  $2.959 \times 10^{-6}$  M pure cis dimer and  $1.988 \times 10^{-6}$  M pure trans dimer (resulting solution = 59.8% trans) was prepared and analyzed as  $2.84 \times 10^{-6}$  M cis and  $1.96 \times 10^{-6}$  M trans (59.2% trans). This indicates that the ultraviolet spectral analysis of unknown mixtures may be expected to be accurate to within 1%.

**Irradiation of Acenaphthylene in Cyclohexane.** All direct irradiations were performed with a 450-W Hanovia medium-pressure mercury arc lamp in a water-cooled Hanovia Vycor immersion vessel fitted with an uranium glass filter sleeve ( $\lambda$  cutoff ca. 330 m $\mu$ ). The solution was contained in an outer Pyrex jacket of approximately 200-ml volume. The solutions were stirred magnetically and the temperature was maintained at about 25°. In all work-up procedures care was taken to maintain a suitable material balance. In all experiments, greater than 94% of the initial sample weight was recovered. A typical run using cyclohexane as solvent is described in detail below.

To 150 ml of cyclohexane (Baker Analyzed or Fisher Certified grades) previously flushed with purified nitrogen was added 15.2 g of acenaphthylene. This solution was irradiated for 15.0 hr with continuous purging with nitrogen. After irradiation the

product was collected by filtration. The vessel was rinsed with boiling benzene (100 ml) which was subsequently evaporated and the resulting residue combined with that obtained by filtration of the original cyclohexane solution. The product was then stirred with cyclohexane (85 ml) in two portions to remove unreacted acenaphthylene, filtered off, and washed with cold cyclohexane (60 ml). After drying in air, 5.62 g of product was obtained (19.42% trans dimer). All cyclohexane filtrates and washings were combined and evaporated to dryness to yield 9.4 g of crude acenaphthylene containing a small amount of the cis dimer due to its solubility in the reaction media.

In order to estimate the amount of this isomer which remains dissolved in the solvent, three methods were employed: column chromatography of the acenaphthylene residue over alumina, vacuum sublimation of unreacted acenaphthylene from the residues, and direct measurements of the solubility of the cis dimer in cyclohexane. The average value from these three methods was 0.30 g of cis isomer per 100 ml of cyclohexane (range, 0.37–0.21 g/ml). This value was therefore used to correct for the solubility of the cis dimer in cyclohexane. Since the trans dimer was found to be approximately fifteen times less soluble than the cis, the slight solubility of the former was neglected.

**The Sensitized Photodimerization of Acenaphthylene.** Sensitized photolyses were performed with methanol solutions of acenaphthylene and sensitizer using a projector equipped with a 750-W Sylvania projector bulb. The light was passed through a glass filter (Corning CS 3-69) which transmitted all wavelengths greater than 510 m $\mu$ . The solution was irradiated in a cell composed of circular quartz plates fused to a quartz tube of the same diameter and approximately 4 cm in length. The total volume was approximately 120 ml. The solutions were continuously purged with purified nitrogen and stirred magnetically. No attempt was made to ensure equal irradiation times or equal quantities of light absorbed.

Except for the length of irradiation all the sensitized irradiations were carried out in an identical manner; a typical sample is given in detail below for the irradiation of acenaphthylene and Rose Bengal.

**Sensitization with Rose Bengal.** With the apparatus previously described, 11.5 g of acenaphthylene dissolved in 115 ml of anhydrous methanol containing 75.1 mg of Rose Bengal ( $7.42 \times 10^{-4}$  M) was photolyzed for 15.0 hr with continuous nitrogen purging. After photolysis the insoluble product was collected by filtration and stirred for 1 hr with methanol (25 ml) to remove residual acenaphthylene and sensitizer. This product mixture was then filtered and stirred for several hours with cyclohexane (25 ml). The methanol filtrates were evaporated to dryness and the acenaphthylene residue was dissolved in cyclohexane (50 ml). No additional dimer remained undissolved in this solution. The product therefore was filtered off, washed with cyclohexane (20 ml), and dried in air to yield 2.63 g of dimer (33.4% cis isomer). A total of 8.88 g of unreacted acenaphthylene was recovered (100% recovery).

**Acknowledgments.** We are grateful to the Public Health Service, National Institute of General Medical Sciences, and the National Science Foundation for financial support.