Anal. Calcd for $C_{10}H_{16}O$: C, 78.90; H, 10.59. Found: C, 78.90; H, 10.69.

Pure 3,5,5-trimethylbicyclo[4.1.0]heptan-2-one (**20**) on a 20% Carbowax 20M column (5 ft × $^1/_4$ in.) was resolved into two peaks, which were assigned as *cis* and *trans* isomers. The first eluted component was 90% of the 3.86 g of distillate with the other accounting for 10%. The above spectral and analytical data were obtained on a sample containing predominantly the first eluted isomer. Ir spectra of the pure isomers had identical carbonyl stretching frequencies (1692 cm^{-1}) and were very similar; however, the fingerprint regions were definitely different. Injection of a 78–22% (first eluted isomer was the 78% one) mixture on a 20% Carbowax 20M–10% KOH column (5 ft × $^1/_4$ in.) gave only one peak. Collection of this peak, and reinjection on a 20% Carbowax 20M column, again gave two peaks in the ratio 75–25%. Repetition of this procedure with a 91–9% mixture gave two peaks on the Carbowax column in the ratio 81–19%. Molecular models indicate the *cis* isomer to be sterically favored.

On the basis of these data, and the irradiation of **20** (see below), the first eluted isomer was assigned the *cis* configuration. A sample largely enriched in the *trans* isomer had the following uv absorption: uv (EtOH) 194 nm (ϵ 3160).

Irradiation of 3,5,5-Trimethylbicyclo[4.1.0]heptan-2-one (20). A solution of 373 mg of a 92–8% mixture of *cis*- and *trans*-3,5,5-trimethylbicyclo[4.1.0]heptan-2-one (**20**) in 125 ml of *t*-butyl alcohol (0.020 *M*) was irradiated for 1.75 hr using Corex-filtered light. Glpc monitoring of the irradiation showed the presence of one major photorearrangement product (retention time relative to *cis* starting material equaled 0.70) as well as an increase in the *trans* isomer of starting material (retention time relative to *cis* starting material equaled 1.20). The final percentages of the total mixture were 20% *cis* starting material, 26% *trans*, 38% major photoproduct, 4% minor photoproducts, and 12% of nonmonomeric material.

Solvent was removed and the major rearrangement product isolated by glpc of the residual, almost colorless oil (376 mg) on a 20% Carbowax 20M column (5 ft × $^1/_2$ in.). This compound was identified as 2,3-methano-4,4-dimethyl-Δ^5-heptenal (**21**) on the basis of the following data: mol wt 152 (mass spectrum); ir (CCl_4) 2857 (w), 2710 (w), 1709 (s), 983 (s), 971 (s) cm^{-1}; uv (EtOH) 220 (ϵ 1830) and 195 nm (ϵ 9610); nmr (τ, CCl_4) 1.18 (1.0 H, doublet, J = 6 Hz, aldehydic H), 4.52–4.75 (1.8 H, four-peak multiplet, vinylic H), 8.14–8.42 (3.8 H, multiplet with a doublet of doublets at 8.33, J = 3 Hz, J' = 2 Hz, one cyclopropyl H and vinylic methyl H), 8.43–9.04 (9.4 H, multiplet with a very strong singlet at 8.88, cyclopropyl H and *gem*-dimethyl H); 100-MHz nmr, the vinyl region was resolved into a multiplet of six peaks, the doublet of doublets at 8.33 was confirmed (J = 3 Hz, J' = 2 Hz), and the singlet at 8.88 was resolved into two singlets separated by 2 Hz.

A spin-decoupling experiment with the 100-MHz nmr gave the following result: irradiation of the 8.33 doublet of doublets collapsed the vinyl absorption to a singlet with two very small satellites at +12.5 and −10.5 Hz away from the singlet; irradiation of the vinyl region collapsed the 8.33 doublet of doublets to a singlet.

Anal. Calcd for $C_{10}H_{16}O$: C, 78.90; H, 10.59. Found: C, 78.66; H, 10.34.

The two geometrical isomers of starting material, after the irradiation, collected together from glpc, gave an nmr spectrum which was identical with that of a sample of starting material containing almost entirely the *cis* isomer. A crude irradiation mixture of **20** containing starting material in the ratio of 52% *cis* to 48% *trans* injected on a 20% Carbowax 20M–10% KOH column (5 ft × $^1/_4$ in.) gave only one peak. Collection of this peak gave an ir spectrum that was essentially identical with that of starting material before irradiation. Reinjection of this peak on a 20% Carbowax 20M column (5 ft × $^1/_4$ in.) again gave two peaks for starting material in the ratio of 74% *cis* to 26% *trans*.

Irradiation of cyclopropyl ketone **20** for 0.75 hr using no filter essentially paralleled the Corex irradiation except that almost everything polymerized. Glpc on a 10% SE-30 column (2$^1/_2$ ft × $^1/_4$ in.) gave no peaks that could be attributed to dimers. This irradiation was not investigated further.

Irradiation in benzene (336 mg, 89% *cis* and 11% *trans*, 125 ml of benzene, 0.018 *M*, Corex filter, 5 hr) essentially paralleled the *t*-butyl alcohol irradiation. The percentages at the end of the irradiation were 29% *cis* starting material, 24% *trans*, 25% 2,3-methano-4,4-dimethyl-Δ^5-heptenal (**21**), 16% of five minor products, and 6% of nonmonomeric material.

Reduction of 2,3-Methano-4,4-dimethyl-Δ^5-heptenal (21). A stirred mixture of 77 mg (0.506 mmol) of 2,3-methano-4,4-dimethyl-Δ^5-heptenal (**21**), glpc collected from the irradiation of 3,5,5-trimethylbicyclo[4.1.0]heptan-2-one (**20**), 10 ml of dry ether, and 0.1 g (2.6 mmol) of lithium aluminum hydride was heated under reflux for 2.5 hr. After the usual work-up, the residual colorless oil (76 mg), greater than 99% pure by glpc, was identified as 2,3-methano-4,4-dimethyl-Δ^5-heptenol (**24**) on the basis of the following data: mol wt 154 (mass spectrum); ir (CCl_4) 3436 (m), 1031 (s), 990 and 984 (both strong) cm^{-1}; ir (CS_2) 975 (m), 787 (s), 766 (s) cm^{-1}; nmr (τ, CCl_4) 4.50–4.77 (1.8 H, six-peak multiplet, vinylic H), 6.44 and 6.46 (1.9 H, two doublets, both J's = 7 Hz, H geminal to hydroxyl), 7.25 (1.0 H, very broad singlet, hydroxy H), 8.35 (3.1 H, doublet of doublets, J = 3.5 Hz, J' = 1.5 Hz, vinylic methyl H), 8.60–9.94 (10.2 H, multiplet with two strong singlets at 8.90 and 8.99, *gem*-dimethyl and cyclopropyl H). A 100-MHz nmr confirmed the above statements.

Anal. Calcd for $C_{10}H_{18}O$: C, 77.87; H, 11.76. Found: C, 77.65; H, 11.86.

The Photodimerization of Acenaphthylene. Heavy-Atom Solvent Effects[1]

Dwaine O. Cowan[2] **and Ronald L. E. Drisko**[3]

Contribution from the Department of Chemistry,
The Johns Hopkins University, Baltimore, Maryland 21218.

Received March 12, 1970

Abstract: The photodimerization of acenaphthylene has been studied in a number of solvents containing heavy atoms. These solvents have been found to promote the formation of triplet-derived products. Correlation of the relative yields of trans dimer with the square of the spin–orbit coupling parameters of these heavy atoms indicate that the heavy-atom solvent effect is a result of spin–orbit coupling.

Heavy atoms (atoms of high atomic number) have been extensively used in the experimental study of radiative and nonradiative molecular processes, either when substituted onto the framework of the molecule of interest or when present in the solvent. Some effects observed in the presence of heavy atoms are: (1)

---

(1) Photochemical Reactions. Part V. Part IV: see D. O. Cowan and R. L. Drisko, submitted for publication.

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

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

Table I. The Dimerization of Acenaphthylene in the Presence of Some Heavy Atoms[a]

Solvent, mol %	Dimer yield, g	Φ_{rel}[b]	cis, g	trans, g	% cis	% trans	cis/trans
n-Butyl chloride							
10	6.60	1.02	5.40	1.20	81.8	18.2	4.50
100	7.14	1.10	5.02	2.12	70.3	29.7	2.37
n-Propyl bromide[c]							
2.5	6.28	0.97	4.91	1.37	78.2	21.8	3.59
5	5.82	0.89	3.74	2.08	64.6	35.4	1.79
10	5.98	0.92	2.53	3.45	42.3	57.7	0.73
25	8.03	1.23	3.00	5.03	37.4	62.6	0.60
50	10.99	1.68	3.50	7.49	31.8	68.2	0.47
100	14.07	2.16	4.06	10.01	28.8	71.2	0.41
Ethyl iodide[c]							
5	10.46	1.61	2.05	8.41	19.6	80.4	0.24
10	13.74	2.11	2.78	10.96	20.2	79.8	0.25
Cyclohexane	6.51	1.00	5.42	1.09	83.2	16.8	4.97
Benzene	9.62	1.48	6.80	2.82	70.6	29.4	2.41

[a] All determinations on 15.2 g of acenaphthylene/150 ml of solvent irradiated for 15.2 hr with nitrogen purging. [b] Relative to the dimerization in cyclohexane. [c] In cyclohexane. [d] Average of five determinations.

increases in phosphorescence quantum yields in rigid matrices; (2) reduction of the phosphorescence lifetime; (3) increases in the strength of absorption bands thought to arise from $T_1 \leftarrow S_0$ transitions; and (4) the quenching of fluorescence.[4] These effects are thought to arise from increased spin–orbit coupling due to interaction of the electronic spin with the highly positively charged nucleus of the heavy atom.[5] This interaction serves to relax the forbiddenness of intercombinational nonradiative ($T_1 \leftsquigarrow S_1$, $S_0 \leftsquigarrow T_1$) and radiative ($S_0 \leftarrow T_1$) processes through "mixing" the singlet and triplet states. The greater the nuclear charge the greater the amount of "mixing" of the states and the transition becomes increasingly more allowed.[6]

Although heavy-atom substituents and solvents have been extensively applied in spectroscopy, few attempts to observe the effect of a heavy atom in a photochemical process have been reported. Wagner has shown[7] that as determined by the type II photoelimination, aliphatic ketones are not sensitive to heavy-atom perturbation. Morrison, *et al.*,[8] have also attempted to observe a heavy-atom effect on the photodimerization of coumarin. Morrison concluded that no firm evidence was obtained for heavy-atom solvent interaction in this case inasmuch as the range of dimer yields in the heavy-atom solvents overlapped the range observed for light-atom solvents.

Both of these cases, however, possess n,π^* excited states which are expected to be relatively insensitive to heavy-atom perturbation since the spin–orbit coupling inherent to the carbonyl function is comparable to or greater than that due to a heavy atom.[9] This has been confirmed by Borkman and Kearns[10] in a study of singlet–triplet absorption in halogen-substituted benzophenones and carboxylic acid bromides.

In an earlier paper in this series we reported the results of mechanistic studies on the photodimerization of acenaphthylene.[11] It was concluded that the cis dimer is formed both from an acenaphthylene excited triplet state and from an acenaphthylene singlet excimer. The trans dimer is formed exclusively (>95%) from the acenaphthylene excited triplet state and therefore should be a sensitive measure of the triplet species concentration under different reaction conditions.

We have reported some preliminary results on the heavy-atom solvent effect on this photodimerization[12] and now describe these results in full and report on results of further research on this solvent effect.

Results

The results of the photolysis of acenaphthylene ($\lambda >$ 330 mμ) in some heavy-atom solvents (*n*-butyl chloride, *n*-propyl bromide, and ethyl iodide) are given in Table I. These results show that heavy-atom solvents exert a noticeable effect on the dimer product distribution (relative to cyclohexane) even when present in rather low concentrations (2.5 mol % *n*-propyl bromide). Increasing the mol % of the heavy-atom solvent in mixed solvents produces an increase in the amount of trans dimer formed.

n-Butyl chloride does not appear to exert a significant heavy-atom effect although the cis/trans ratio for this solvent (2.37) is less than half that for the irradiation in pure cyclohexane (4.97). This former value is very similar to the dimer ratio for benzene (2.41). It appears therefore that *n*-butyl chloride behaves as a "light-atom" solvent and exerts an effect similar to that observed for other such solvents. Ethyl iodide on the other hand is seen to exert an effect considerably greater than *n*-propyl bromide, a 5 mol % solution being remarkably effective in promoting the formation of the trans dimer.

---

(4) (a) D. S. McClure, *J. Chem. Phys.*, 17, 905 (1949); (b) M. Kasha, *ibid.*, 20, 71 (1952); (c) M. Z. Hoffman and G. Porter, *Proc. Roy. Soc., Ser. A*, 268, 46 (1962); (d) M. R. Padaye, S. P. McGlynn, and M. Kasha, *J. Chem. Phys.*, 24, 588 (1956); (e) S. P. McGlynn, R. Sunseri, and N. Christodouleas, *ibid.*, 37, 1818 (1962); (f) S. P. McGlynn, M. J. Reynolds, G. W. Daigre, and N. D. Christodouleas, *J. Phys. Chem.*, 66, 2499 (1962); (g) S. P. McGlynn, J. Daigre, and F. J. Smith, *J. Chem. Phys.*, 39, 675 (1963); (h) S. Siegel and H. J. Judeikis, *ibid.*, 42, 3060 (1965).

(5) W. Kauzmann, "Quantum Chemistry," Academic Press, New York, N. Y., 1957.

(6) (a) S. K. Lower and M. A. El-Sayed, *Chem. Rev.*, 66, 199 (1966); (b) M. A. El-Sayed, *Accounts Chem. Res.*, 1, 8 (1968).

(7) P. J. Wagner, *J. Chem. Phys.*, 45, 2335 (1966).

(8) H. Morrison, H. Curtis, and T. McDowell, *J. Amer. Chem. Soc.*, **88**, 5415 (1966); H. Morrison and R. Hoffman, *Chem. Commun.*, 453 (1968).

(9) M. A. El-Sayed, *J. Chem. Phys.*, 41, 2462 (1964).

(10) R. F. Borkman and D. R. Kearns, *J. Chem. Phys.*, 46, 2333 (1967).

(11) D. O. Cowan and R. L. Drisko, *Tetrahedron Lett.*, 1255 (1967); D. O. Cowan and R. L. Drisko, submitted for publication.

(12) D. O. Cowan and R. L. Drisko, *J. Amer. Chem. Soc.*, 89, 3068 (1967).

Table II. The Dimerization of Acenaphthylene in Other Heavy-Atom Solvents[a]

Solvent, mol %	Dimer yield, g	cis, g	trans, g	% cis	% trans
Neopentyl bromide[b]					
5.4	6.41	3.84	2.57	59.9	40.1
10	6.81	2.81	4.00	41.3	58.7
Bromobenzene[b]					
10	5.53	2.81	2.72	50.8	49.2
Tri-*n*-butylantimony[b]					
5	5.13	3.50	1.89	64.9	35.1
Tetra-*n*-butyltin[b]					
10	5.29	4.20	1.09	79.4	20.6
Tetraphenyllead[c]					
0.5	4.27	3.55	0.72	88.1	11.9
Ethylene dibromide[b]					
10	6.11	1.81	4.30	29.6	70.4
Carbon tetrachloride	5.52	2.79	2.72	50:5	49.5

[a] All determinations on 15.2 g of acenaphthylene/150 ml of solvent for 15.0 hr. [b] In cyclohexane. [c] In benzene.

The results of the photodimerization in other heavy atom containing solvents are presented in Table II. It is seen that some of these compounds also serve to enhance the yield of trans dimer relative to cyclohexane. Difficulty was encountered in the use of the metal complexes, tri-*n*-butylantimony and tetraphenyllead, owing to the instability of the former and the insolubility of the latter. Consequently, the results of these two photolyses are expected to be considerably low. The results of the experiments using carbon tetrachloride and ethylene dibromide indicate that the number of heavy atoms substituted onto the perturbing molecule is important in determining the relative amount of trans dimer formed. The yield of trans dimer is increased by a factor of 1.25 by the presence of the second bromine atom in ethylene bromide as compared to propyl bromide (10 mol %). The yield of trans in carbon tetrachloride is increased by a factor of 1.31 relative to the yield in *n*-butyl chloride.

Discussion and Conclusions

We have shown that the trans dimer is formed exclusively from triplet-excited acenaphthylene. Since this triplet state must be populated through intersystem crossing from the singlet manifold, any increase in the efficiency of this forbidden process might be expected to result in a higher yield of the trans dimer. However, before this conclusion can be reached the heavy-atom effect on all spin-forbidden processes must be considered. These processes, in addition to intersystem crossing from the lowest singlet to the lowest triplet state (k_{isc}), are light absorption to form the triplet state directly (I_a), phosphorescence from the triplet state (k_p), spin relaxation of a triplet intermediate ($k_{2\text{-t}}$ and $k_{2\text{-c}}$), and intersystem crossing from the lowest triplet to the ground state (k_d), where the notation is the same as that used in our earlier papers.[11]

$$\mathrm{A^s} \xrightarrow{k_{\mathrm{isc}}} \mathrm{A^t} \qquad (1)$$

$$\mathrm{A} + h\nu \xrightarrow{I_a} \mathrm{A^t} \qquad (2)$$

$$\mathrm{A^t} \xrightarrow{k_p} \mathrm{A} + h\nu \qquad (3)$$

$$\begin{tikzcd}
\mathrm{A^t} + \mathrm{A} \arrow[r] & {[\uparrow \mathrm{A{-}A} \uparrow]^t} \arrow[r, "k_{2\text{-t}}", "k_{2\text{-c}}"'] \arrow[d, "k_{q'}"] & \mathrm{A_2}\text{(trans or cis)} \qquad (4) \\
 & 2\mathrm{A} &
\end{tikzcd}$$

$$\mathrm{A^t} \xrightarrow{k_d} \mathrm{A} \qquad (5)$$

The importance of light absorption to directly populate the triplet state in the presence of heavy atoms and the effect of heavy atoms on the phosphorescence of acenaphthylene are easily ruled out. No new absorption bands (reaction 2) or increased band intensities are noted over the heavy-atom acenaphthylene concentration ranges studied. Since no phosphorescence is observed, even at low temperature, there cannot be an important effect on this process (reaction 3). Spin relaxation to increase the rate of product formation (reaction 4) was discussed in an earlier paper and shown not to be an important process.[11] This leaves two processes occurring from the excited acenaphthylene molecule which may be affected by heavy-atom perturbation (reactions 1 and 5).

The first process serves to populate the triplet state; the other to depopulate it. Thus if the heavy atom were to increase k_d more than it increases k_{isc}, the yield of triplet-derived products would decrease. Since the probability of a singlet–triplet transition resulting from spin–orbit coupling depends inversely upon the energy separation between the two states, one would expect a greater probability of crossing from a perturbed excited singlet to the triplet state than from the perturbed triplet to the ground state.[6,13] Since an increase in triplet-derived products is observed it appears that k_{isc} is more sensitive to the perturbation than k_d. A note of caution should be injected at this point since this conclusion is only valid if unimolecular decay (k_d) is the main nonproduct-forming route leading to the depopulation of the triplet state. If bimolecular quenching ($k_{q'}$; reaction 4) is more important than unimolecular decay by several orders of magnitude, k_d could be increased as much or more than k_{isc} without serving to decrease the steady-state triplet population. Indeed, an increase in the triplet-derived product would still be observed. Consequently, although k_{isc} appears to be more sensitive than k_d to the heavy atom, this is not necessarily the case since bimolecular self-quenching of the triplet acenaphthylene molecule is probably more important than unimolecular decay. In both the case where (a) the heavy atom increases k_{isc} much more than it does k_d and in the case where (b) the heavy atom increases both k_{isc} and k_d but the resultant k_d is still small compared to $k_{q'}[\mathrm{A}]$, *only the heavy-atom effect on* k_{isc} *is mirrored in the triplet-derived products.*

The external heavy-atom solvent effect on the probability (P) of a nonradiative transition can be explained by postulating that the singlet and triplet states of the solute and solvent are mixed by the formation of an encounter complex (exchange interaction). One formulation for this process is given below[6,13,14]

$$P \propto \langle A^{\mathrm{s}}|H'|A^{\mathrm{t}}\rangle^2 = \frac{\langle A^{\mathrm{s}}|H^{\mathrm{I}}|{}^1\psi_{\mathrm{solv}}{}^{\mathrm{a}}\rangle^2\langle {}^1\psi_{\mathrm{solv}}{}^{\mathrm{a}}|H_{\mathrm{so}}|{}^3\psi_{\mathrm{solv}}{}^{\mathrm{b}}\rangle^2\langle {}^3\psi_{\mathrm{solv}}{}^{\mathrm{b}}|H^{\mathrm{II}}|A^{\mathrm{t}}\rangle^2}{\Delta E_{\mathrm{a}}\Delta E_{\mathrm{b}}}$$

where A^{s} and A^{t} are the wave functions for the acenaphthylene singlet and triplet states and ${}^1\psi_{\mathrm{solv}}{}^{\mathrm{a}}$ and ${}^3\psi_{\mathrm{solv}}{}^{\mathrm{b}}$ are the corresponding functions for singlet and triplet

---

(13) S. P. McGlynn, T. Azumi, and M. Kinoshita, "The Triplet State," Prentice-Hall, Englewood Cliffs, N. J., 1969.

(14) G. W. Robinson and R. Frosch, *J. Chem. Phys.*, 37, 1962 (1962); 38, 1187 (1963).

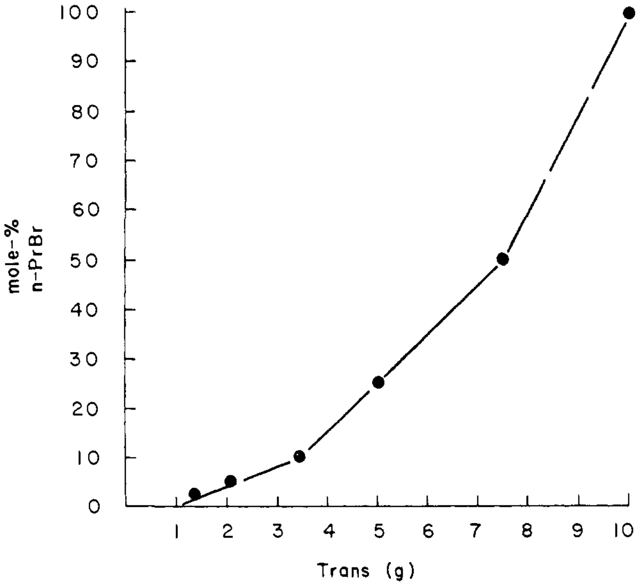

Figure 1. Amount of trans dimer formed as a function of solvent composition (*n*-propyl bromide, cyclohexane). All irradiations were performed on 15.2 g of acenaphthylene/150 ml of solvent for a period of 15.2 hr.

states of the solvent that mix with A^s and A^t. H_{so} is the spin–orbit Hamiltonian and H^I and H^{II} are operators that result from the breakdown of the Born–Oppenheimer approximation. Other formulations involving perturbed acenaphthylene singlet and triplet states can be written but they all indicate that for a similar group of perturbing solvents the probability of the transition is proportional to the square of the spin–orbit Hamiltonian and therefore to the square of the spin–orbit coupling parameter.

$$P \propto |H_{so}|^2 \propto \zeta^2$$

Assuming that the spin–orbit coupling parameter for the heaviest atom in the perturbing molecule constitutes the total perturbation, the ratio of the probability of a given process in the presence of one heavy atom to that in the presence of another is approximated by

$$\frac{P_1}{P_2} = \frac{\zeta_1^2}{\zeta_2^2}$$

The spin–orbit coupling parameters of some heavy atoms are given in Table III.

Table III. Spin–Orbit Coupling Parameters of Some Heavy Atoms[a]

Atom	δ, cm^{-1}
Cl	587
Sn	2097
Br	2460
Sb	3400
I	5060
Pb	7292

[a] E. U. Condon and G. H. Shortley, "Theory of Atomic Spectra," Cambridge University Press, London, 1935.

Use of this heaviest atom type of approximation has been made by McClure[4a] and by McGlynn, *et al.*,[4f] in studies of radiative transitions (absorption and phosphorescence) for various halogen-substituted molecules. Order of magnitude correlations were obtained.

In the photodimerization of acenaphthylene such a dependence on the spin–orbit parameter of the heavy-atom solvent should be reflected in the ratio of the amount of trans dimer formed in one heavy-atom solvent to that formed in another. That is

$$\text{trans}_1/\text{trans}_2 = \zeta_1^2/\zeta_2^2$$

The data in Tables I–III have been used to calculate these ratios for some of the heavy atoms used. The results are summarized in Table IV.

Table IV. Comparison of the trans Dimer Ratio with the Ratio of the Squares of the Spin–Orbit Coupling Parameters

Solvents	$\zeta_{\text{heavy}}^2/\zeta_{\text{I}}^2$	trans (heavy)/trans (I)[a]
Ethyl iodide[b]	1	1
n-Propyl bromide[b,c]	0.24	0.24
Neopentyl bromide[b]	0.24	0.29
Neopentyl bromide[d]	0.24	0.20
Bromobenzene[b]	0.24	0.17
n-Butyl chloride[b]	0.104	0.01
Tri-*n*-butylantimony[d]	0.45	0.25

[a] It is assumed that the presence of 5–10 mol % of the heavy-atom solvent exerts no effect other than that through spin–orbit coupling. Therefore, the trans dimer yield in these solvents has been corrected for the amount of trans formed in pure cyclohexane. [b] 10 mol % heavy-atom solvent in cyclohexane. [c] Only the calculation based on 10 mol % heavy-atom solvent is given inasmuch as the results of 5 mol % of this solvent were erratic. [d] 5 mol % heavy-atom solvent in cyclohexane.

It is seen that these ratios agree well, especially in the bromide and chloride cases. We conclude that the heavy-atom solvents increase the rate of intersystem crossing *via* spin–orbit coupling.

Some variation in these ratios as a function of the structure (R–X) of the heavy atom containing molecule might be expected since the probability stealing from the environment is reported to be proportional to the fourth power of the intermolecular molecular orbital overlap integral[13] and depends inversely upon the energy separation (ΔE_a, ΔE_b) of the acenaphthylene and solvent singlet and triplet states.[6] The best comparison should be, and in fact is, between similar heavy-atom solvents (EtI, *n*-PrBr, *n*-BuCl).

In addition, variation in these ratios as a function of the structure of the heavy atom containing molecule might be expected in light of Schenck's report[15] and our work regarding the sensitivity (to solvent) of the dimer distribution obtained from the monomeric triplet state. That is, this state produces both dimeric products (with the trans dimer strongly predominating) but the ratio of the two products depends upon the ability of the solvent to stabilize the transition states leading to the dimers. Even better agreement may have been obtained in Table IV if it were possible to directly compare the total dimer product derived from this triplet reaction.

Increasing the mol % of the heavy-atom solvent in the solvent mixture produced a concurrent increase in the amount of trans dimer formed, as can be seen in

---

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

Figure 1. This plot is observed to be essentially linear in the region between 10 and 50 mol % propyl bromide. For higher mole percentages of the heavy-atom solvent, the dimer yield is practically quantitative.

Carbon tetrachloride appears to have a significantly greater effect on the relating trans–cis dimer yields than does *n*-butyl chloride. When compared with *n*-propyl bromide, the trans dimer yield corresponds to a heavy-atom effect where $\zeta = 1.28 \times 10^3$ cm^{-1}, or to an average ζ of 320 cm^{-1} per chlorine atom in the perturbing molecule. Thus, an atom with as low a spin–orbit coupling parameter as Cl ($\zeta = 587$ cm^{-1}) can exert a heavy-atom effect if a sufficient number of such atoms are present in close proximity.

In a study of the singlet–triplet absorption spectra of α-halonaphthalenes, McGlynn, *et al.*,[4e] proposed that the observed absorption strength was dependent upon the relative acceptor ability of the organic halide used as solvent. The electron-acceptor tendency of some of the alkyl halides used in this study increased as isobutyl < *n*-propyl < ethyl < methyl. The change in oscillator strength for the α-halonaphthylene singlet–triplet absorption in these alkyl iodides increased in a parallel order. This correlation was interpreted to mean that the external heavy-atom effect arose through the formation of weak donor–acceptor complexes. Such complexes cannot be a predominant factor in the photodimerization of acenaphthylene since the expected order of the bromides (bromobenzene < neopentyl bromide < *n*-propyl bromide) was not observed.

The data in Table II show that tetra-*n*-butyltin exerts no heavy-atom effect on the dimerization although tin has a spin–orbit coupling parameter of 2097 cm^{-1}. This may be due to the crowded geometry of this molecule if the bulky butyl groups prevent the heavy atom from approaching within the minimum distance necessary for its effect to be observed. A similar effect has been observed for the quenching of the fluorescence of riboflavin by iodide ion. At pH's where this molecule bears a negatively charged phosphate[16] the iodide ion is repelled and cannot approach close enough to affect the fluoresence.

It can be seen that the heavy-atom effect, so commonly used in spectroscopy, can also be an important tool in photochemistry, not only to facilitate the study of a reaction mechanism but also to control the major reaction product. The product control would be very useful if a synthetically desired photoproduct, formed in a minor yield, could be made the major product through the use of a heavy-atom solvent.[17] We also suggest that this effect may prove useful in studying the mechanism of heavy-atom perturbation.

Experimental Section

The photolysis apparatus methods of product analysis have been previously described. A uranium glass filter sleeve (cut off *ca.* 330 mμ) was used in all cases. The solutions were continuously purged with purified nitrogen during the irradiation period. All heavy-atom solvents were found to absorb less than 0.05% of the light at 365 mμ. *n*-Butyl chloride was Fisher Reagent grade. *n*-Propyl bromide was obtained from Eastman Kodak. Ethyl iodide was a Fisher product and was distilled directly before use. Tri-*n*-butylantimony and tetra-*n*-butyltin were from Alfa Inorganics. Tetraphenyllead was from the International Lead-Zinc Research Organization. Neopentyl bromide was prepared by the method of Wiley, *et al.*,[18] and was distilled before use.

Acknowledgments. We are grateful to the Public Health Service, National Institute of General Medical Sciences, and to the National Science Foundation for financial support and acknowledge material support by The International Lead-Zinc Research Organization, Inc., New York, N. Y., through the Institute for Organic Chemistry TNO, Utrecht, The Netherlands.

(16) B. Holmstrom and L. Tegner, *Photochem. Photobiol.*, **5**, 207 (1966).

(17) After the preparation of this manuscript there appeared a paper making use of the heavy-atom perturbation of acenaphthylene to increase the rate of photoaddition of acenaphthylene to acrylonitrile: B. F. Plummer and R. A. Hall, *Chem. Commun.*, 44 (1970).

(18) G. A. Wiley, R. L. Hershkowitz, B. M. Rein, and B. C. Chung, *J. Amer. Chem. Soc.*, **86**, 964 (1964).