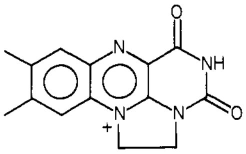
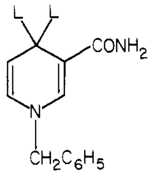
the three examples studied, ~1.07.

Discussion

The foregoing results show no sign of the change in primary KIE which would suggest a multistep mechanism.[3] The observed primary KIE's are not far below the value, 6.9, given by the Eyring and Cagle approximation[17] for the conversion of a 2800-cm^{-1} frequency of the reactant to the reaction coordinate. An even wider range of equilibrium constants can be obtained by considering the reaction of the substituted flavin, **8**, with 1-benzyl-1,4-dihydronicotinamide (**9**), for which Powell and Bruice have very recently reported a primary KIE of 4.06, measured in acetonitrile.[7] (The structure of **8** has been drawn in a somewhat unorthodox manner, to emphasize its similarity to the other oxidizing agents of our series.) From the redox potentials given by Powell and Bruice a K of 10^{16} can be estimated for this reaction. For a one-step reaction with λ of 72 kcal mol^{-1},[2] Marcus' theory of atom transfer would suggest that a primary KIE of 5.40 for a K of 1.0 would fall to 5.28 for a K of 2×10^6 and 4.7 for a K of 10^{16}.[18] Considering the scatter, the uncertainty in the equilibrium constant for the reaction of **8** and **9**, and the possible solvent effect on the KIE, these predictions are in reasonable accord with the observations. All these primary KIE values are, therefore, entirely consistent with the one-step model of the hydride transfer.[2]



8



9

It is somewhat harder to fit the secondary KIE's into this picture. The conversion of an sp^2-hybridized C–H bond to sp^3 hybridization is expected to produce a small *inverse* KIE. The equlibrium isotope effect (EIE) on the reduction of NAD$^+$ to NADH (isotopic substitution of H at the 4-position) is expected to be 0.89.[19] The transition states for the present reactions appear to be close to symmetrical, both structurally and energetically, so that in the absence of dynamic coupling, a secondary KIE of ~0.95 might have been expected. This is approached for deuterium transfer, but for hydrogen transfer k_H/k_D is larger than 0.95 by 5–8 times the uncertainty of the experimental result. Results presenting similar difficulties have previously been found by Kurz and Frieden for the non-enzymic reduction of 4-cyano-2,6-dinitrobenzene sulfonate by NADH[20] and by Cleland and co-workers[21] for a number of enzymic reductions by NADH. The secondary KIE values can be accommodated by assuming strong coupling between the in-place and the in-flight hydrogens. However, since this involves several atomic motions in the reaction coordinate, it leads to calculated primary KIE values much below those observed. The dilemma can be resolved by allowing nuclear tunneling in the reaction coordinate. In that case less coupling is required, because some of the secondary KIE is provided by increasing the mass in the reaction coordinate when the in-place hydrogen is isotopically substituted. Also, the primary KIE is amplified by the tunneling. As a bonus, the diminuation of the secondary KIE when deuterium is in-flight is explained, because in that case, tunneling will be much less important. All of this has been quantified, and our results have been substantially rationalized.[22] In a model calculation intended to mimic the reaction of NADH with acetaldehyde, but including motion of the in-place hydrogen in the reaction coordinate and substantial tunneling, Huskey and Schowen obtained a primary KIE of 5.5, a secondary KIE of 1.17 with H in flight, and a secondary KIE of 1.06 with D in flight. These results depend strongly on the inclusion of tunneling. We therefore conclude that the model is correct.

Registry No. **1**·I, 948-43-6; **2**, 4217-54-3; **3a**, 30319-92-7; **3b**, 87861-94-7; **3c**, 87861-95-8; **4a**·I, 50741-48-5; **4c**·Br, 87861-96-9; **5a**·I, 5412-06-6; **5c**·Br, 87861-99-2; **6**, 719-54-0; **7a**, 4594-73-4; **7b**, 87861-97-0; **7c**, 87861-98-1; 3-cyanoquinoline, 34846-64-5; phenanthridine, 229-87-8; 3-cyano-1,4-dihydro-1-methylquinoline, 72594-76-4; deuterium, 7782-39-0; 4CF$_3$C$_6$H$_4$CH$_2$Br, 402-49-3; PhCH$_2$Br, 100-39-0.

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Energetics of Twisting in the Lowest Stilbene Triplet State[1]

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Abstract: The temperature dependence of the azulene effect on the benzophenone-sensitized photoisomerization of the stilbenes is reported in toluene, benzene, *tert*-butyl alcohol, and acetonitrile. The data are consistent with formation of identical stilbene triplets from the two stilbene isomers. Predictions concerning the shape of the potential energy curve for twisting about the central bond depend on the detailed mechanism assumed for the quenching interaction. A lower enthalpy for the twisted triplets is predicted, $\Delta H_{tp} = -2.1$ and -1.6 kcal/mol in toluene and *tert*-butyl alcohol, respectively, if it is assumed that the equlibrium population of transoid triplet geometries, $^3t^*$, is negligible and that quenching follows encounters of twisted stilbene triplets, $^3p^*$, with azulene when they achieve $^3t^*$ geometries in the encounter cage. On the other hand, if quenching is assumed to occur only by direct interaction between $^3t^*$ and azulene, equilibrium constants for the $^3t^* \rightleftarrows {}^3p^*$ process are obtained which predict a lower enthalpy content for transoid triplets: $\Delta H_{tp} = 0.5$ and 2.9 kcal/mol for toluene and *tert*-butyl alcohol, respectively. In the latter case entropy is predicted to favor twisted geometries so that for both mechanisms the free energy favors $^3p^*$ at the temperatures normally employed for photochemical studies. Reasons for favoring the $^3p^*$ quenching mechanism are presented.

Structural preferences of 1,2-diarylethene triplets in solution have been inferred from consequences of their interactions with quenchers. Encounter of olefin triplets in planar (or nearly so) conformations with molecules having lower lying triplet states results in triplet excitation transfer with concomitant formation of the corresponding ground-state olefin isomer. On the other hand, molecules with non-zero electronic spin (e.g., ground-state O_2, or di-*tert*-butyl nitroxide) promote intersystem crossing from twisted (orthogonal with respect to the central bond) geometries of olefin triplets giving trans and cis ground states in nearly the same ratio as does unperturbed radiationless decay.[2]

Judicious use of both types of quenchers has revealed that in the case of the stilbenes transoid, $^3t^*$, and twisted, $^3p^*$, conformations are accessible energetically following relaxation of initially formed triplets.[3] In particular, excitation transfer to azulene gives *trans*-stilbene by interaction with $^3t^*$,[3a,d] an effect strongly attenuated by molecular oxygen, which by opening a new decay channel from $^3p^*$ shortens the effective stilbene triplet lifetime.[3c,d] When neither planar geometry is energetically accessible to the relaxed olefin triplet the excitation-transfer pathway does not operate. An example of this case is provided by the α-methylstilbenes (1,2-diphenylpropenes) in which the steric requirements of the methyl group raise the energy of transoid geometries.[3a]

Complementary information concerning preferred geometries of 1,2-diarylethene triplets stems from the functioning of ground-state isomers as acceptors of energy from low triplet energy, E_T, donors.[2,3a] Endothermic triplet excitation transfer rate constants from a series of donors with varying E_T to *trans*-stilbene seem to fit a model requiring little or no distortion of the acceptor during the transfer step (vertical transfer), whereas rate constants for *cis*-stilbene and both 1,2-diphenylpropenes suggest substantial geometry changes in the acceptors concomitant with the transfer step (nonvertical transfer).[4] This behavior is accommodated readily if one assumes that a transoid geometry, corresponding to a minimum on the triplet energy surface, provides entry to that surface when *trans*-stilbene accepts triplet excitation, but that no such minimum exists on the cis side for stilbene, or on either isomer side for the 1,2-diphenylpropenes. Lacking such a minimum, the latter, upon accepting triplet excitation, enter the triplet potential energy surface at or near an energy minimum at the perpendicular geometry. While these conclusions are substantially in harmony with those based on the quenching observations, the notion that *trans*-stilbene is a vertical acceptor of triplet excitation is not entirely consistent with activation parameters obtained with anthracene as the donor.[5,6] Thus, though the behavior of the stilbenes as acceptors of triplet excitation is in agreement with the conclusion that transoid geometries are energetically accessible to the stilbene triplet, it fails to establish that such geometries represent a minimum in the potential energy surface. Even if such a minimum existed, the average transoid triplet geometry may differ substantially from that of ground-state *trans*-stilbene. Assignment of transient triplet–triplet absorption spectra of *p*-nitrostilbenes to $^3t^*$ has been based convincingly on the insensitivity of these spectra to large temperature and medium changes.[7] However, a similar conclusion drawn for stilbene itself was based on much more ambiguous spectral evidence.[3d]

Table I. The Azulene Effect on Benzophenone-Sensitized Stilbene Photostationary States

T, K	[Az] × 10^2, M	$(t/c)_s$[a]	*T*, K	[Az] × 10^2, M	$(t/c)_s$[a]
Benzene[b]					
303.2	0	0.690 (4)	303.2	2.22	2.50 (4)
	1.13	1.61 (4)		2.44	2.78 (1)
	1.45_7	2.08 (3)		3.33	3.57 (2)
Toluene[c]					
303.2	0	0.62 (2)	274	2.05	2.22 (1)
	1.04_2	1.69 (1)		2.77	2.73 (3)
	2.08_4	2.63 (6)	195	0	0.85_5
	3.12_6	3.48 (9)			
tert-Butyl Alcohol[d]					
303.2	0	0.81 (4)	303.2	2.44	4.65 (9)
	0.79_0	1.99 (1)		3.07	5.66 (6)
	1.51_4	3.44 (3)			
Methanol[e]					
303.2	0	0.75_4 (6)	303.2	1.52	3.69 (8)
	0.75_6	2.11 (5)		2.27	5.16 (9)
n-Pentane[f]					
303.2	0	0.59 (1)	270	0	0.61 (3)
	0.75_1	1.75 (3)		1.02	2.23 (4)
	1.50	3.17 (2)		2.04	3.68 (5)
	2.46	4.91 (4)		3.05	5.43 (6)
Acetonitrile[g]					
303.2	0	0.70_4 (5)	303.2	2.24	4.11 (17)
	0.74_7	1.80 (4)		2.99	4.94 (4)
	1.50	2.89 (7)			

[a] Values in parentheses are experimental uncertainties in last decimal place(s) from GLC analyses. [b] [B] = 0.0486 M, [St] = 0.0304 M (48.5% t), 250-μL aliquots. [c] T = 303.2 K; [B] = 0.0493 M, $[St]_0$ = 0.0137 M (71.7% t). T = 274 and 195 K: [B] = 0.0499 M, [St] = 0.10 M PSS bracketed, 250-μL aliquots. [d] [B] = 0.047 M, [St] = 0.0176 M (52.3% t). [e] [B] = 0.0099 M, [t] = 1.72×10^{-2} M. [f] T = 303.2 K: [B] = 0.040 M, t = 0.0199 M. T = 270 K: [B] = 0.044 M, t = 0.013 M, 250-μL aliquots. [g] [B] = 0.020 M, [St] = 0.020 M (50% t).

The shape of the potential energy surface for twisting about the central bond in the lowest stilbene triplet has been the subject of numerous theoretical calculations.[8] The purpose of the present work is to provide an experimental estimate for the energetics of $^3t^* \rightleftarrows {}^3p^*$ equilibration from a determination of the temperature dependence of the efficiency of the azulene effect on the triplet (benzophenone-sensitized) pathway to stilbene photoisomerization.

Results

The effect of azulene on trans/cis photostationary-state ratios, $(t/c)_s$, for the benzophenone-sensitized photoisomerization of the stilbenes was measured in several solvents (Table I).[9] These measurements were carried out at 30.0 °C except in the cases of toluene and *n*-pentane where a temperature close to 0 °C was also employed. The temperature dependence of the azulene effect was determined in toluene, *tert*-butyl alcohol, and acetonitrile by using Whitten and Lee's quantum yield method (Table II).[10] Similar, but more qualitative, results were obtained in *n*-pentane. In this method azulene effects of internal filtering and quenching of sensitizer triplets are compensated for by employing actinometry solutions in which *trans*-1,2-diphenylpropene is substituted for the stilbenes. Since the absence of azulene quenching of 1,2-diphenylpropene triplets had only been demonstrated in hydrocarbon solvents, it was necessary to carry out control experiments in alcoholic media where unexpectedly large azulene effects on

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(1) (a) Supported by National Science Foundation Grants No. GP-24265 and CHE 80-26701. (b) A preliminary report on this work has appeared: Saltiel, J.; Chang, D. W.-L.; Megarity, E. D.; Rousseau, A. D.; Shannon, P. T.; Thomas, B.; Uriarte, A. K. *Pure Appl. Chem.* **1975**, *41*, 559.

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Table II. The Azulene Effect on Benzophenone-Sensitized Stilbene Photoisomerization Quantum Yields[a]

T, K	[Az] × 10^2,[b] M	$\phi_{t\to c}$[c]	*T*, K	[Az] × 10^2,[b] M	$\phi_{t\to c}$[c]
		Toluene[d]			
$332._5$	0	0.54_7 (0.53_9)	$273._2$	2.05	0.29_1 (0.75_9)
	1.92	0.20_8 (0.84_5)		3.07_4	0.24_5
$304._0$	0	0.55_6 (0.41_6)	$243._7$	0	0.56_3[e]
	1.98	0.24_8 (0.85_3)		0	0.54_0 (0.48_2)
$303._4$	0.99_2	0.35_6		2.11	0.37_0 (0.68_4)
	1.98_4	0.24_6		2.11	0.35_6[e]
$302._7$	0	0.51_5 (0.44_6)	$243._5$	1.05_7	0.44_0
	1.98	0.24_4 (0.76_8)		2.11_3	0.37_2
$273._2$	0	0.55_0 (0.50_6)		3.17_0	0.31_3
	0	0.53_8 (0.48_8)	228.4	0	0.52_9
	1.02_5	0.42_5		0	0.52_9 (0.46_3)
	2.04_9	0.28_8		2.14_5	0.39_0[e]
	2.05	0.28_6 (0.77_8)		2.14_5	0.38_1 (0.61_5)
		tert-Butyl Alcohol[f]			
$353._2$	0	0.55_9	317.7	0	0.55_8
	0	0.57_1		0.94_8	0.28_6
	0.90_0	0.25_3[g]		0.97_3	0.27_9
	0.92_3	0.22_3		1.89_7	0.19_5
	1.80_0	0.16_8[g]		1.94_6	0.19_6
	1.84_6	0.15_5	303.2	0	0.56_6
$334._7$	0	0.56_4		0	0.56_3
	0.92_5	0.25_6		0.96_8	0.31_2
	0.94_9	0.25_8		0.99_3	0.33_1
	1.85_0	0.17_5[g]		1.93_7	0.22_0[g]
	1.89_7	0.15_6		1.98_7	0.21_6
		Acetonitrile[h]			
$333._5$	0.94_7	0.27_6	$258._9$	2.10_1	0.26_1
	1.89_5	0.17_3		3.15_2	0.20_5
	2.84_2	0.13_1	$233._3$	1.08_6	0.42_3
$313._3$	0.97_6	0.30_1		2.17_1	0.32_3
	1.95_2	0.18_2		3.25_7	0.23_6
	2.92_9	0.13_9			
$283._6$	1.01_7	0.30_8			
	2.03_4	0.24_2			
	3.05_2	0.15_4			

[a] Multiple entries for the same [Az] and *T* represent entirely independent experiments. [b] [Az] adjusted for changes in density with *T*. [c] Values in parentheses are $\phi_{c\to t}$. [d] Benzophenone, ~0.050 M (~23 °C), throughout; stilbene, 0.100 M, where ϕ's are given for both directions, and otherwise 0.0180 M, except as noted. [e] Stilbene, 0.100 M. [f] Benzophenone, 0.020 M; stilbene, 0.0180 M. [g] Mean from duplicate samples, deviation from mean ≤2.3%. [h] Benzophenone, 0.050 M; stilbene 0.0180 M.

Table III. The Azulene Effect on Benzophenone-Sensitized 1,2-Diphenylpropene Photoisomerization Quantum Yields in *tert*-Butyl Alcohol, 30 °C[a]

[Az] × 10^2, M	$\phi_{t\to c}$	$\phi_{c\to t}$
0	0.53_7	0.46_3
1.00	0.55_6	0.44_4
2.00	0.53_5	0.46_5

[a] Initial 1,2-diphenylpropene concentrations, 0.0187 M; benzophenone, 0.0200 M; conversion range 2.05-3.40%.

stilbene triplets have been reported. Relative quantum yields for benzophenone-sensitized isomerization of the 1,2-diphenylpropenes in both directions were measured as a function of [Az] in *tert*-butyl alcohol at 30 °C (Table III). Isomerization conversions were converted to quantum yields (Table III) by assuming $\phi_{t\to c} + \phi_{c\to t} = 1.00$ and that the two isomers of 1,2-diphenylpropene compete equally with azulene for benzophenone triplets.[4b] As an additional check stationary states for the 1,2-diphenylpropenes were measured under the same conditions (*tert*-butyl alcohol, 30 °C) and were found to be essentially independent of [Az]: 44.6 ± 0.4% trans, [Az] = 0; 45.4 ± 0.1% trans, [Az] = 0.0200 M.

Discussion

We begin with the simplest mechanism for sensitized stilbene photoisomerization (Scheme I) where $^3St^*$ represents common stilbene triplets of unspecified geometry. Such a mechanism is consistent with the observation of identical triplet–triplet stilbene absorption spectra when either isomer is excited by high triplet energy donors.[3d] According to Scheme I, for benzophenone-sensitized stilbene photoisomerization, $K_{az} = k_{az}/k_d$ values can be calculated either from the response of $(t/c)_s$ to [Az],

$$(t/c)_s = (k_c/k_t)[\alpha/(1-\alpha)](1 + K_{az}[Az]/\alpha) \qquad (1)$$

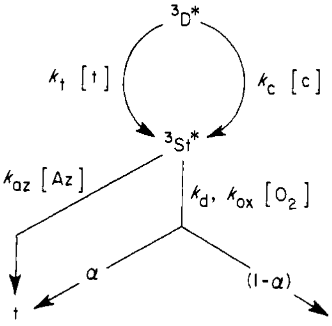
or from the response of isomerization quantum yields to [Az],

$$\phi_{t\to c}^{-1} = (1-\alpha)^{-1}(1 + K_{az}[Az]) \qquad (2)$$

$$\phi_{c\to t}^{-1} = (1 + K_{az}[Az])/(\alpha + K_{az}[Az]) \qquad (3)$$

Values of K_{az} obtained by applying eq 1 with $\alpha = 0.45$ on the data in Table I and eq 2 on the data in Table III are shown in Table IV. The use of $\alpha = 0.45$ is in agreement with the best quantum yield values for sensitized stilbene photoisomerization found in the literature.[11] It also coincides with the average value of α obtained in this work using eq 2 in toluene and *tert*-butyl alcohol throughout the temperature range, $\alpha = 0.449 \pm 0.010$ for 228.4 K ≤ *T* ≤ 353.2 K (Table IV). Since quantum yields were not measured in the absence of azulene in acetonitrile, the value of $\phi_{t\to c} = 0.55$ for [Az] = 0 was included as an assumed point in going from the data in Table II to the K_{az} values in Table IV. Also shown in Table IV are K_{az} values from experiments described in the literature. These values deviate somewhat from those previously reported because $\alpha = 0.45$ was applied throughout instead of using the earlier procedure which allowed small variations in α but required that the rate constants for triplet excitation transfer from benzophenone to the stilbenes, k_c and k_t, be exactly equal.

Scheme I. The Common Stilbene Triplet Mechanism



A thorough discussion leading to the conclusion that a common triplet mechanism best explains all steady-state and transient observations involving stilbene triplets in fluid solution has been presented recently.[3d] Scheme I has also been shown to apply to other 1,2-diarylethene triplets, most notably, perhaps, to the 1-phenyl-2-(2-naphthyl)ethenes for which a significant red shift of triplet–triplet absorptions allowed confirmation of the steady-state azulene experiments[12] by transient decay measurements.[13] The results presented here provide additional evidence firmly establishing Scheme I. First, it can be seen from the quantum yields in toluene (Table II) that $\phi_{c\to t} + \phi_{t\to c} = 1$, within experimental uncertainty, independent of [Az] and of *T*. This finding is consistent with eq 2 and 3, which require that the decrease in $\phi_{t\to c}$ caused by azulene be accompanied by a complementary increase in $\phi_{c\to t}$, and it is also consistent with the observation of identical stilbene triplet–triplet transient absorption spectra starting with either stilbene isomer.[3d] Second, application of eq 1 and 2 to stationary-state and quantum-yield observations, respectively, gives entirely self-consistent K_{az} values (Table IV) in all solvents employed, as required by Scheme I. This is especially noteworthy in the case of *tert*-butyl alcohol for which conflicting stilbene triplet transient decay observations have been reported.[3d,14] The identity

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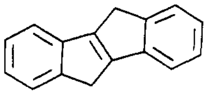
Table IV. Stilbene Triplet Kinetic Parameters

T, K	K_{az},[a] M^{-1}	$k_{dif} \times 10^{-9}$,[b] $M^{-1}\,s^{-1}$	$p \times 10^2$ [c]	$K_{tp}k_d \times 10^{-8}$, s^{-1}	K_{tp}[c]	$k_d \times 10^{-7}$, s^{-1}	method[d] (ref)
Benzene							
$333._2$	$87._0$	15.1	9.29	1.74	9.7_6	1.7_8	S (9a)
$333._2$	$86._3$	15.1	9.2_2	1.75	9.8_5	1.7_8	S (9c)
$303._2$	$55._1$	9.5_3	9.3_3	1.73	9.7_3	1.7_8	S
$301._2$	$55._1$	9.2_2	9.6_4	1.67	9.3_7	1.7_8	S (3a)
$298._2$	$54._3$	8.7_5	10.0_1	1.61	8.9_9	1.7_9	S (9a)
$298._2$	$52._2$	8.7_5	9.6_2	1.68	9.3_9	1.7_9	S (9c)
Toluene							
$332._5$	$84._9$ (0.54_7)	15.5	8.8_3	1.82	10.3	1.7_7	Q
$303._4$[e]	$60._6$ (0.54_4)	10.4	9.4_0	1.72	9.6_4	1.7_8	Q
$303._2$	$60._7$	10.4	9.4_1	1.71	9.6_2	1.7_8	S
274	$41._5$	6.4_2	10.4_3	1.55	8.5_9	1.8_0	S
$273._2$	$42._8$ (0.55_5)	6.3_3	10.9_1	1.48	8.1_7	1.8_1	Q
$243._6$[f]	$24._0$ (0.55_1)	3.4_3	11.2_9	1.43	7.8_6	1.8_2	Q
$228._4$	$17._4$ (0.55_9)	2.3_6	11.8_9	1.36	7.4_1	1.8_4	Q
$303._2$[g]	154	$30._4$	8.6_6	1.98	10.6	1.8_7	S
270[g]	118	$20._2$	9.9_9	1.72	9.0_4	1.9_0	S
tert-Butyl Alcohol							
$353._2$	$133._0$ (0.54_6)	18.4	11.2_1	1.38	7.9_5	1.7_4	Q
$334._7$	$131._2$ (0.57_1)	12.7	16.0_2	0.96_8	5.2_4	1.8_5	Q
$317._7$	$93._1$ (0.54_3)	8.7_1	16.5_7	0.93_6	5.0_4	1.8_6	Q
$303._2$	$82._0$ (0.57_1)	6.1_0	20.8_4	0.74_4	3.8_0	1.9_6	Q
$303._2$	$79._2$	6.1_0					S (9b)
$303._2$	$85._5$	6.1_0					S (9b)
$303._2$	$81._5$	6.1_0	20.7_1	0.74_8	3.8_2	1.9_6	S[h]
$303._2$[i]	$124._2$	15.2[j]	13.5_1	1.22	6.4_0	1.9_1	S
Acetonitrile							
$333._5$	$113._1$	$21._1$	9.0_1	1.8_7	10.1	1.8_5	Q
$313._3$	$100._6$	$17._8$	9.5_0	1.7_7	9.5_3	1.8_6	Q
$303._2$	$88._8$	$16._3$	9.1_6	1.8_4	9.9_5	1.8_5	S
$283._6$	$77._5$	$13._3$	9.7_9	1.7_2	9.2_3	1.8_6	Q
$258._9$	$53._3$	9.9_7	8.9_8	1.8_7	10.1	1.8_5	Q
$233._3$	$37._5$	6.9_0	9.1_3	1.8_4	9.9_5	1.8_5	Q

[a] Values in parentheses are $(1 - \alpha)$ values from intercepts of plots, eq 2. [b] Interpolated values from ref 15; benzene values based on toluene data adjusted for T/η. [c] Based on τ = 62.0, 64.5, 60.5, 59.5 and 58.5 ns for benzene/toluene, *tert*-butyl alcohol, methanol, acetonitrile, and *n*-pentane, respectively; see ref 3d and text. [d] S, eq 1; Q, eq 2; this work unless otherwise indicated. [e] Data for 302.7–304.0 K treated together. [f] Data for 243.5 and 243.7 K treated together. [g] Solvent is *n*-pentane. [h] Data from ref 9b and this work treated together. [i] Solvent is methanol. [j] Estimated from ref 3d and 15.

of the K_{az} values obtained from eq 1 and 2 in this solvent is consistent with the observation of a common triplet stilbene transient from *cis*- and *trans*-stilbene,[3d] rather than of two separate transients, $^3p^*$ and $^3t^*$, whose equilibration is incomplete even after 50 ns following the excitation pulse.[2,14] More explicitly, the results reported in ref 14 for *tert*-butyl alcohol appear to be close to the limiting case of $^3t^* \xrightarrow{k_{tp}} {}^3p^* \nrightarrow {}^3t^*$ which requires that plots of stationary-state and quantum-yield observations give identical slope/intercept ratios equal to k_{az}/k_{tp} instead of K_{az}/α and K_{az}, respectively, as observed and as expected from Scheme I, eq 1, and eq 2. The observations in ref 14 may reflect complications, such as exciplex formation, specific to β-acetonaphthone, the sensitizer employed.

The nearly inverse dependence of K_{az} on solvent viscosity in aprotic solvents had led to the suggestion that the rate constant for triplet excitation transfer from transoid triplets to azulene is diffusion controlled.[1b,9b] Experimental confirmation of this conclusion was provided by a careful flash-kinetic determination of rate constants, k_i, for triplet excitation transfer from the rigid *trans*-stilbene analogue indeno[2,1-*a*]indene (I) to azulene.[15]



I

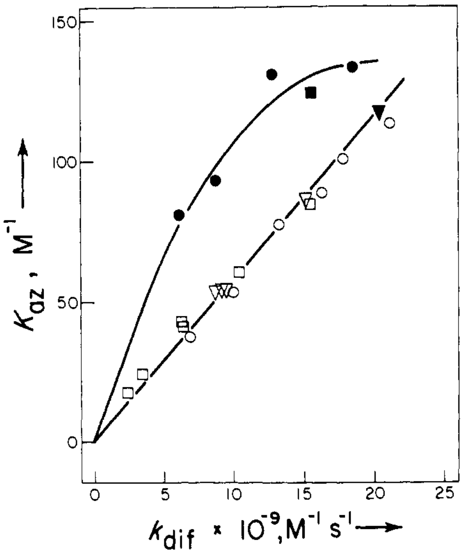


Figure 1. Dependence of K_{az} on k_{dif}: (□) toluene, (▽) benzene, (○) acetonitrile, (▼) *n*-pentane, (●) *tert*-butyl alcohol, (■) methanol.

Comparison of k_i values with *tert*-butyl radical termination rate constants[16] convincingly showed that the excitation-transfer process is fully diffusion controlled, $k_i = k_{dif}$, under all conditions employed. Inter- and extrapolated values of k_i are listed as k_{dif} in Table IV.

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(14) Sumitani, M.; Yoshihara, K.; Nagakura, S. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 2503.

(15) Saltiel, J.; Shannon, P. T.; Zafiriou, O. C.; Uriarte, A. K. *J. Am. Chem. Soc.* **1980**, *102*, 6799.

(16) Schuh, H.-H.; Fischer, H. *Helv. Chim. Acta*, **1978**, *61*, 2130.

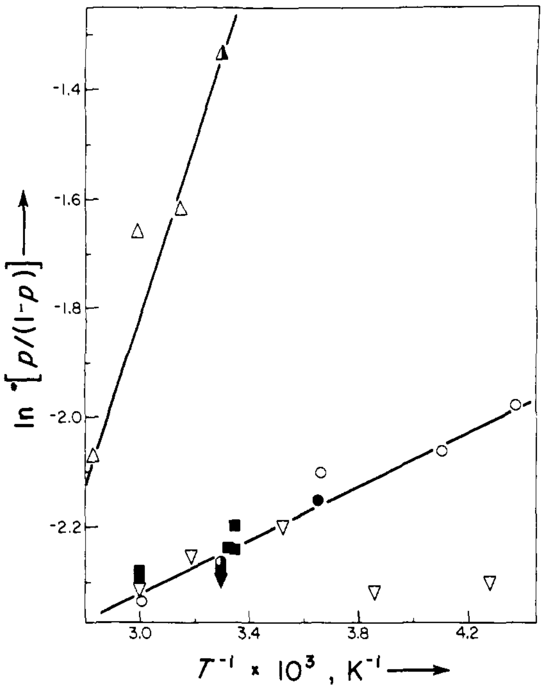


Figure 2. Data treatment based on Scheme I: (□) benzene, (○) toluene, (▽) acetonitrile, (△) *tert*-butyl alcohol; open symbols from quantum yields, closed symbols from photostationary states, half-filled symbols from both quantum yields and photostationary states.

Except for the data in the alcohol solvents, the k_{az} values are a linear function of k_{dif} (Figure 1). If k_{az} in Scheme I were indeed fully diffusion controlled, the slope of the line in Figure 1, ~5.5 ns, would be the predicted, nearly temperature independent, lifetime of stilbene triplets. Since the observed lifetime, though temperature independent,[3d] is more than 10 times larger than this value, the mechanism in Scheme I must be modified to account for the inefficiency in k_{az}. The simplest modification involves including explicitly the competition between energy transfer and diffusion apart which follows $^3St^*$ encounters with Az. Back energy transfer from $^3Az^*$ to t can be neglected since it is highly endothermic (eq 4). It follows that K_{az} in eq 1–3 equals

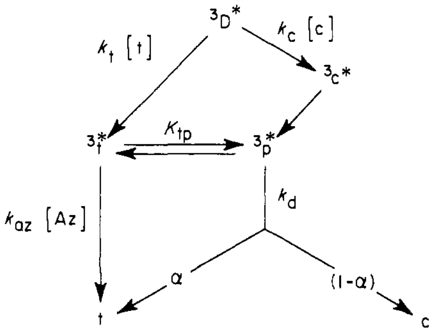
$$^3St^* + Az \underset{k_{-dif}}{\overset{k_{dif}}{\rightleftharpoons}} (^3St^*Az) \xrightarrow{k_{en}} (t^3Az^*) \xrightarrow{k_{-dif}} t + {}^3Az^* \qquad (4)$$

$k_{dif}k_{en}/k_d(k_{en} + k_{-dif})$ so that $k_{az} = k_{dif}k_{en}/(k_{en} + k_{-dif})$, and the slope of the line in Figure 1 gives pk_d where $p = k_{en}/(k_{en} + k_{-dif})$ is the fraction of $^3St^*/Az$ encounters that lead to excitation transfer. Görner and Schulte-Frohlinde, in a nicely complementing study, have shown that τ is temperature independent (25 to ~70 °C) and nearly solvent independent, ranging from 57 to 65 ns in all solvents employed in this work except toluene.[3d] In the case of toluene, the significantly higher τ values obtained exhibited an unexpected and unexplained dependence on the sensitizer employed to produce stilbene triplets: xanthone 77–80 ns; benzophenone 67–70 ns.[3d] In view of these anomalies, the τ value obtained in benzene (62 ± 1 ns)[3d] was assumed for toluene. Individual p values based on these lifetimes (Table IV) are plotted according to

$$\ln [p/(1 - p)] = \ln (k_{en}/k_{-dif}) = \ln (A_{en}/\xi A_\eta) + (E_\eta - E_{en})/RT \qquad (5)$$

where $k_{-dif} = \xi k_{-dif} = \xi A_\eta \exp(-E_\eta/RT)$ in Figure 2. The values for benzene and *n*-pentane are close to the line defined by the toluene points that gives $(E_\eta - E_{en}) = 0.49$ kcal/mol and $(A_{en}/\xi A_\eta) = 4.7 \times 10^{-2}$. The acetonitrile p values appear to be temperature independent over the 100 °C range employed. However, inspection of Figure 2 shows that four of the six acetonitrile points also fall close to the toluene line. Since the acetonitrile data are the least extensive, it would not be surprising if the two lowest temperature points in this solvent are in error. The *tert*-butyl alcohol data define a different line which gives $(E_\eta - E_{en}) = 2.84$ kcal/mol and $(A_{en}/\xi A_\eta) = 2.4 \times 10^{-3}$. If the enthalpy change for the formation of the encounter pair in eq 4 is negligible, ξ = [S], the molarity of the solvent, can be calculated from the entropy change (cratic) for bringing two solutes together.[15] Values of ξ, being proportional to solvent density, change by 10% over the temperature ranges employed. Activation parameters for k_{en} were calculated from the lines in Figure 2 with the use of average ξ values and known empirical activation parameters for k_{dif}:[15] log A_{en} = 11.63, 11.55 and E_{en} = 2.23, 1.86 kcal/mol for toluene and *tert*-butyl alcohol, respectively. Somewhat lower values are obtained if the temperature dependence of ξ is accounted for by plotting ln $[\xi p/(1 - p)]$ vs. $1/T$: log A_{en} = 11.50, 11.34 and E_{en} = 2.07, 1.55 kcal/mol for the same solvents.

Scheme II. Transoid and Twisted Stilbene Triplets in Equilibrium



Interpretation of k_{en}. Since the chemical consequence of the interaction of stilbene triplets with azulene is formation of trans ground-state isomer, exclusively, more detailed mechanisms converge on the same final step: excitation transfer from transoid triplets to azulene. The mechanism considered initially[3] and the one favored in the most recent literature[3d] assumes rapid $^3t^* \rightleftharpoons {}^3p^*$ equilibration in solution with triplet excitation occuring very efficiently only when transoid triplets interact with a suitable acceptor (Scheme II). Interactions of $^3p^*$ with the acceptor are assumed not to contribute significantly and are neglected. Though this mechanism guided the design of the experiments described in this paper, its relationship to the data will be considered last. We examine first an alternative mechanism, more closely related to Scheme I, in which the azulene effect has its origin in $^3p^*$ encounters with Az. It was based on the observation of efficient quenching of stilbene triplets by oxygen that does not alter $(t/c)_s$ ratios and suggests that at equilibrium stilbene triplets exist predominantly in $^3p^*$ geometries.[1b] In the original formulation of this mechanism (Scheme I, with $^3St^* = {}^3p^*$) it was proposed that the initial encounter was followed by rapid $^3p^* \rightleftharpoons {}^3t^*$ equilibration in the presence of azulene with excitation transfer occuring only from $(^3t^*Az)$ pairs:

$$^3p^* + Az \underset{k_{-dif}}{\overset{k_{dif}}{\rightleftharpoons}} (^3p^*Az) \underset{k_{tp}}{\overset{k_{pt}}{\rightleftharpoons}} (^3t^*Az) \xrightarrow{k_{en}'} (t^3Az^*) \xrightarrow{k_{-dif}} t + Az^* \qquad (6)$$

The modified version in eq 6 shows explicitly the excitation-transfer step that was inadvertently omitted in the published version. Application of the steady-state approximation to all excited species, including encounter pairs, leads to eq 1–3 with

$$K_{az} = (k_{dif}k_{pt}k_{en}')k_d^{-1}[k_{-dif}(k_{tp} + k_{en}') + k_{pt}k_{en}]^{-1} \qquad (7)$$

It follows that the parameter p defined above is now given by $p = k_{pt}k_{en}'[k_{-dif}(k_{tp} + k_{en}') + k_{pt}k_{en}']^{-1}$. The limiting case of complete $^3p^*$, $^3t^*$ equilibration within the encounter cage requires $k_{tp} \gg k_{en}'$, leading to $K_{az} = (k_{dif}k_{pt}k_{en}')k_d^{-1}(k_{-dif}k_{tp} + k_{pt}k_{en}')^{-1}$, which replaces eq 17 in ref 1b. It follows that for this limit $p = k_{pt}k_{en}'(k_{-dif}k_{tp} + k_{pt}k_{en}')^{-1}$ which can be rearranged to $p/(1 - p) = k_{en}'K_{pt}/k_{-dif}$. Comparison of this expression with the one used in eq 5 shows that, for the fast equilibration limit, k_{en} in Scheme I is replaced by $k_{en}'K_{pt}$. It follows that the activation parameters obtained above for k_{en} include enthalpy and entropy changes for the $^3p^* \rightleftharpoons {}^3t^*$ twisting process. Since acceptors ranging from β-carotene,[3c] $E_T \simeq 21$ kcal/mol, to 1,2-benzanthracene, $E_T \simeq$

47 kcal/mol, all quench stilbene triplets to the trans isomer with about the same efficiency as azulene, $E_T \simeq 39$ kcal/mol, it seems reasonable to assume that the $^3p^* \rightarrow {}^3t^*$ distortion gives nearly planar transoid triplets whose excitation energy is above 47 kcal/mol and may be as high as 49 kcal/mol, the well-established spectroscopic E_T of $^3t^*$. Accordingly, k_{en}' being the rate constant for a highly exothermic triplet excitation transfer, should have zero, or nearly so, activation energy. The activation energies for k_{en}' are therefore associated with the enthalpy change for the twisting process: $\Delta H_{pt} = 2.1$, 1.6 kcal/mol in toluene and *tert*-butyl alcohol, respectively. Since the enthalpy change is a good measure of the change in potential energy, this result predicts that the energy of the transoid triplet which transfers excitation lies about 2.1 kcal/mol higher in energy than the relaxed twisted state and that alcoholic solvents reduce this energy difference by ~0.5 kcal/mol. If, furthermore, entropy favors $^3p^*$, as is likely, the predicted enthalpy differences are consistent with the assumption that $^3p^*$ is the predominant stilbene triplet in solution, even if one assumes that the proximity of the quencher does not affect the thermodynamic parameters for $^3p^*$, $^3t^*$ equilibration. A possible flaw in this mechanism is the requirement that k_{en}' be considerably smaller than the corresponding rate constant for I. Barring formation of a triplet exciplex between $^3I^*$ and Az, the conclusion that excitation transfer is faster than diffusive separation in as fluid a solvent as *n*-pentane suggests that for I $k_{en} \geq 2 \times 10^{12}$ s^{-1}.[15] If k_{en}' in the ($^3t^*$Az) pair were this large it would be unlikely that k_{tp}, the rate constant for $^3t^* \rightarrow {}^3p^*$ conversion could far exceed this value as is required for complete torsional equilibration to be achieved in the encounter cage.

For very large $k_{en}' \gg k_{tp}$, the $^3p^* \rightarrow {}^3t^*$ process becomes the rate-limiting step for excitation transfer, and eq 7 simplifies to $K_{az} = (k_{dif}k_{pt}k_{en}')k_d^{-1}(k_{-dif}k_{en}' + k_{pt}k_{en}')^{-1}$ from which $p/(1-p) = k_{pt}/k_{-dif}$ can be derived. For this "slow torsion" limit k_{en} in Scheme I is replaced by k_{pt} and the activation parameters derived above are associated with this rate constant: $\log A_{pt} = 11.50$, 11.34 and $E_{pt} = 2.07$, 1.55 kcal/mol for toluene and *tert*-butyl alcohol, respectively. The enthalpy of activation for this process can be obtained from $\Delta H_{pt} = E_{pt} - RT = 1.5$ and 1.0 kcal/mol in the same order, values which again suggest considerable stabilization (~0.5 kcal/mol) of transoid geometries relative to twisted geometries by the alcoholic medium (or destabilization of $^3p^*$ relative to $^3t^*$). It should be noted that $\log A_{pt} = 11.3$ is in excellent agreement with the value assigned to $\log A_{tp}$ for the $^1t^* \rightarrow {}^1p^*$ process of *trans*-1,2-di-3-pyridylethene in *tert*-butyl alcohol.[17]

$^3t^*$ Quenching Mechanism. We return to the two-triplet mechanism of Scheme II which predicts $K_{az} = k_{az}/K_{tp}k_d$ in eq 1–3. In this case, k_{az} is defined as the rate constant for the quenching of transoid triplets by azulene, and K_{tp} is the equilibrium constant for the $^3t^* \rightleftharpoons {}^3p^*$ process in the absence of a neighboring azulene molecule. Accepting $^3I^*$ as a reasonable model for $^3t^*$, we can set $k_{az} = k_i = k_{dif}$ and can calculate $K_{tp}k_d$ values from K_{az} by using $K_{tp}k_d = k_{dif}/K_{az}$ (Table IV). The reasoning which had led to the conclusion that the azulene effect on stilbene triplet decay is initiated by $^3p^*$/azulene interaction was, in part, based on the mistaken notion that the effective stilbene triplet lifetime predicted by Scheme II is given by $(K_{tp}k_d)^{-1}$.[1b] The long stilbene triplet lifetimes inferred from the attenuation of the azulene effect by oxygen[1b,3c] and, more precisely later, by direct transient kinetics studies[3d] while seemingly in disagreement with the $K_{tp}k_d$ values, can be accommodated by the correct expression for the stilbene triplet lifetime:[3d,18]

$$\tau = (1 + K_{tp})/K_{tp}k_d \tag{8}$$

K_{tp} and k_d values, uniquely defined by the $K_{tp}k_d$ parameter (Table IV) and transient lifetimes,[3d] are also listed in Table IV. It can be seen that the rate constant for $^3p^* \rightarrow {}^1p$ decay is predicted within experimental uncertainty to be remarkably solvent and temperature independent, $k_d = 1.8 \pm 0.1 \times 10^7$ s^{-1}, whereas the equilibrium constant for $^3t^* \rightleftharpoons {}^3p^*$ equilibration, K_{tp}, shows a modest solvent dependence and, especially in *tert*-butyl alcohol, a modest dependence on temperature changes. Plots of the toluene/benzene and *tert*-butyl alcohol K_{tp}'s (Figure 3) show satisfactory adherence to

$$\log K_{tp} = -\frac{\Delta H_{tp}}{2.303RT} + \frac{\Delta S_{tp}}{2.303R} \tag{9}$$

giving ΔH_{tp} values of 0.46 ± 0.04 and 2.86 ± 0.44 kcal/mol and ΔS_{tp} values of 5.99 ± 0.14 and 12.1 ± 1.4 eu in toluene/benzene and *tert*-butyl alcohol, respectively. The acetonitrile K_{tp} values appear to be temperature independent over the 100 °C range employed, and as expected application of eq 9 gives $\Delta H_{tp} = -0.021 \pm 0.75$ kcal/mol and $\Delta S_{tp} = 4.46 \pm 0.27$ eu. However, as with the previous models, inspection of Figure 3 shows that four of the six acetonitrile points are close to the benzene/toluene line. The single K_{tp} value in methanol falls between the two lines. Thus, application of Scheme II to the data leads to the conclusion that enthalpy and, therefore, potential energy, since $P\Delta V$ can be neglected, favor transoid geometries, $^3t^*$ (slightly, ~0.5 kcal/mol in hydrocarbon solvents, and more decisively, ~2.9 kcal/mol, in *tert*-butyl alcohol), while entropy favors twisted, $^3p^*$, geometries. The lowering of the enthalpy content of $^3t^*$ in *tert*-butyl alcohol is compensated, in part, by an increase of the entropy of $^3p^*$ in that solvent.

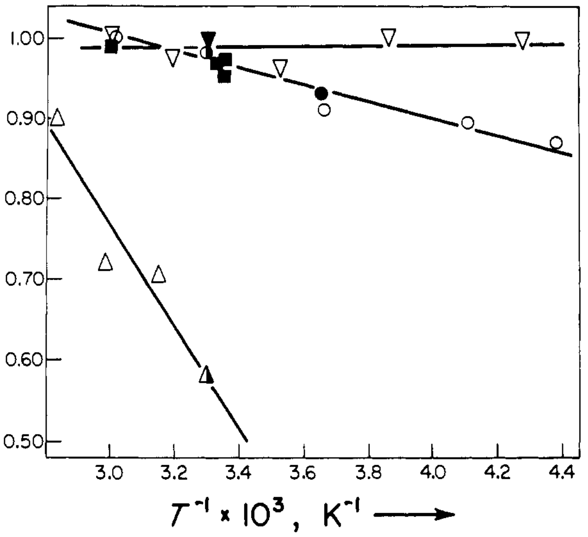


Figure 3. Data treatment based on Scheme II, symbols as in Figure 2.

Table V. Enthalpy Changes for $^3t^* \rightleftharpoons {}^3p^*$

	ΔH_{tp}, kcal/mol	
model	$C_6H_5CH_3$/ C_6H_6	*t*-C_4H_9OH
Scheme I[a]	−2.1	−1.6
Scheme II	0.5	2.9

[a] With $^3St^*$ taken as $^3p^*$, for the fast equilibration limit in the presence of the quencher.

Critical Summary. Although the conclusion that, for stilbene, $^3p^*$ geometries predominate at equilibrium at the temperatures normally employed for photochemical studies does not depend on the quenching mechanism, predictions, based on different mechanisms, concerning the shape of the triplet potential energy curve along the torsional coordinate differ sharply (Table V). If quenching is assumed to be initiated solely when $^3p^*$ encounters Az, Scheme I with $^3St^* \equiv {}^3p^*$, the temperature dependence of K_{az} leads to the prediction that $^3p^*$ is somewhat lower in enthalpy (or potential energy) than $^3t^*$. The opposite conclusion is reached if it is assumed that quenching occurs only when $^3t^*$ encounters Az.

Following a detailed discussion of the pros and cons of the two Schemes, Görner and Schulte-Frohlinde came to the conclusion

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(17) Saltiel, J.; D'Agostino, J. T. *J. Am. Chem. Soc.* **1972**, *94*, 6445.

(18) This expression is analogous to one considered for stilbene singlet decay:[2] (a) Birch, D. J. S.; Birks, J. B. *Chem. Phys. Lett.* **1976**, *38*, 432. (b) Charlton, J. L.; Saltiel, J. *J. Phys. Chem.* **1977**, *81*, 1940.

that the $^3t^* \rightleftharpoons {}^3p^*$ equilibrium used in Scheme II best accounts for all the observations.[3d] Crucial in their considerations is the assignment of the transient triplet–triplet stilbene absorption to $^3t^*$. This assignment, however, is not as convincing as in the case of *p*-nitrostilbenes for which transient triplet–triplet spectra are relatively independent of temperature.[7] In the case of stilbene the low temperature spectrum with well-defined absorption bands at ~380, ~360, and ~340 nm is replaced at room temperature by a broad absorption which seems to reach a maximum at ~360 nm.[3d] I, on the other hand, which is constrained to the transoid geometry, retains its long wavelength absorption, ~390 nm, at room temperature.[3d] Possibly, measurement of the triplet–triplet absorption spectrum of 1,2-diphenylpropene whose relaxed triplet state is expected to exist only in the $^3p^*$ geometry will allow a more definitive assignment of the geometry(ies) of the triplets responsible for the room temperature stilbene spectrum. But, even if 10–30% of stilbene triplets were present as $^3t^*$ in solution as required by the K_{tp} values which were based on Scheme II (Table IV), some quenching of $^3p^*$ by Az via the $(^3p^*Az) \rightarrow (^3t^*Az)$ process cannot be ruled out. Of relevance here are studies designed to determine whether this $^3p^* \rightarrow {}^3t^*$ conversion within the initial encounter cage can trigger the functioning of a quantum chain mechanism for *cis*-stilbene isomerization sensitized by low triplet energy sensitizers. Limiting $\phi_{c\rightarrow t}$ values 16–20% larger than expected in the absence of this process were obtained with 1,2-benzanthracene and 1,9-benzanthr-10-one as sensitizers.[19] This modest increase suggests that though the predominant fate of ($^3p^*$Az or S) pairs is diffusive separation, twisting to $^3t^*$ occurs as a competing process. Mercer-Smith and Whitten have shown that such a quantum chain process operates more efficiently when palladium and platinum porphyrins, P, are used as sensitizers of *cis*-stilbene photoisomerization.[20,21] In these systems formation of a relatively long-lived donor/acceptor triplet exciplex probably allows the $(^3p^*P) \rightarrow (^3t^*P)$ conversion to come prominently into play. It should also be noted that the mechanism in Scheme II does not easily lend itself to an understanding of the high $(t/c)_s$ ratios obtained when anthracenes are employed as sensitizers of stilbene photoisomerization in alcohol solvents.[22,23]

Our own observations concerning activation parameters for endothermic triplet excitation transfer to the stilbenes using anthracene and 9,10-dichloroanthracene as donors suggest strongly that the *transfer is nonvertical for both isomers*.[5] Accordingly, it appears that distortion toward $^3p^*$ from either cisoid or transoid triplet geometries is accompanied by a decrease in potential energy (and therefore enthalpy). This conclusion is consistent with the $^3p^*$ quenching mechanism of Scheme I which we consequently favor at this time.

Independent of which mechanism applies *tert*-butyl alcohol is predicted to shift the enthalpy difference between $^3t^*$ and $^3p^*$ by favoring the $^3t^*$ side. The fact that the K_{az} values for acetonitrile do not deviate significantly from the values in hydrocarbon solvents (Figure 1) shows that the change in the energy parameters in *tert*-butyl alcohol should be associated with solvent–solvent and/or solute–solvent hydrogen bonding interactions and not with increased solvent polarity. Whatever the origin of the effect, the use of variable amounts of *tert*-butyl alcohol in benzene as a means of studying the effect of solvent viscosity on the interaction of stilbene triplets with 9,10-diphenylanthracene was an unfortunate solvent choice.[23]

Theoretical calculations on the shape of the potential energy curve for rotation about the central double bond in the lowest triplet state of stilbene abound.[8] Practically every conceivable shape for this curve has been predicted and previous work has been critically reviewed.[8] We hope that the present contribution will aid future theoretical efforts.

Experimental Section

Materials. Methanol (Matheson Coleman and Bell, reagent grade) was distilled over Mg under an atmosphere of nitrogen. The middle cut, bp 64.7 °C, was used. All other solvents were either identical with those used in the related experiments with I[15] or purified by the same procedures. Sources and purification of the stilbenes, benzophenone, and azulene were as previously described.[9b,d] Initial isomer compositions were ≤0.10% *cis*- in *trans*-stilbene and ≤0.36% *trans*- in *cis*-stilbene (GLC). A 1:1 mixture of the 1,2-diphenylpropenes (GLC) was prepared from acetophenone (Eastman), benzyl bromide (Aldrich), and triphenylphosphine (Eastman) by using the Wittig reaction (81% yield). Samples of pure cis and trans isomers, obtained by chromatography on alumina, showing negligible contamination by the other isomer (GLC), were employed in all *tert*-butyl alcohol experiments and those quantum yield experiments in toluene which were performed in both directions. The *trans*-1,2-diphenylpropene used in the remaining experiments contained 0.42% cis isomer.

Irradiation Procedures. Most stationary-state experiments were carried out with a Moses merry-go-round apparatus immersed in a thermostated water bath, 30.0 °C, as previously described.[9b,d] A 450-W Hanovia medium-pressure mercury lamp, L679A, was employed. For quantum-yield experiments and photostationary-state measurements at lower temperatures identical sample preparation and degassing procedures were employed, but irradiation ampules were prepared from 3.0-mm o.d. Pyrex tubing, contained 250-μL aliquots, and were irradiated in a small cylindrical merry-go-round attached to a stirring motor (Gerald K. Heller Co., Model G.T. 21). The small merry-go-round, 2.15-cm o.d. anodized aluminum holding up to six ampules, was immersed in a Pyrex Dewar containing water or methanol, copper coils, and two calibrated alcohol thermometers. Light from an Osram HBO 200-W super-high-pressure lamp was collimated and then made to converge on the sample tubes by using a Bausch and Lomb housing and appropriate lenses. The temperature in the Dewar was regulated by circulating a liquid (water or methanol) through the copper coils with a Haake type FS constant temperature circulator. For experiments below 0 °C a heat exchanger containing CO_2/isopropyl alcohol was also employed. The rate of flow through the heat exchanger was controlled with bypass valves. A combination of Corning CS 7-37 and 0-52 glass color filters was employed throughout to isolate the group of mercury lines at 366 nm.

Analytical Procedures. Determination of isomeric compositions was by GLC on a Varian Aerograph Series 2700 gas chromatograph, as previously described.[9] Recorders were equipped with disk integrators. In several instances ratios of azulene to the stilbenes and of benzophenone to the stilbenes were determined and shown to be independent of irradiation time. The stability of azulene under the irradiation conditions was also confirmed by recording visible absorption spectra on a Cary 14 spectrophotometer.

Quantum Yield Calculations. The six sample positions of the small merry-go-round were calibrated periodically by irradiating sets of identical *trans*-stilbene solutions in parallel. The average deviation between corrected conversions for samples in such sets never exceeded ±5%. Stilbene solutions containing benzophenone and varying amounts of azulene were irradiated in parallel with identical solutions in which *trans*-1,2-diphenylpropene was substituted for stilbene. Conversions, corrected for zero-time isomeric contamination and hole calibration factor, were employed to obtain an approximate set of quantum yields with $\phi = 0.54$ for *trans*-1,2-diphenylpropene.[3a,10,11b,24] These approximate quantum yields were plotted vs. [Az] according to eq 2 and approximate K_{az} values obtained which were used to calculate $(t/c)_s$ ratios as a function of [Az] and *T*. These stationary states were used in order to correct the initial conversions for back-reaction.[9d,24] Hole calibration factors were applied next and final ϕ's calculated. Final K_{az} values did not differ significantly from corresponding approximate K_{az}.

Registry No. Stilbene, 588-59-0; azulene, 275-51-4; 1,2-diphenylpropene, 779-51-1.

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