

perature at which there is only one inflection point on either side of the maximum (inflection definition). For cases in which the equilibrium constant is near one (**2a**, **2b**, **2c**, and **2d**) these two definitions refer to the same signal shape; however, when the populations differ greatly from one (**2e**, **2f**, and **2g**), the two definitions correspond to different signal shapes and coalescence temperatures. When the equilibrium constant was substantially different from one, we chose the minimum definition. Rate constants at coalescence (by either definition) were determined by a complete line-shape method, and hence the free energies of activation reported are independent of the definition used.

N-Alkyl-*N*-arenesulfonylsulfenamides (**2**). The title compounds were prepared by reaction of the appropriate *N*-alkylsulfenamides with butyllithium followed by reaction with the appropriate sulfenyl chlorides as previously described.⁷ Physical properties and analytical data are given in Table IV.

Kinetic Measurements. The rate constants (Table III) used to determine the activation parameters for **2a** were obtained using two methods. The low-temperature (−65 to −48°) rate constants were determined by conventional kinetics of equilibration as previously described.¹¹ The high-temperature (28–92°) rate constants were obtained by complete line-shape analysis.

Mechanism of Direct *Cis*–*Trans* Photoisomerization of the Stilbenes. Solvent Viscosity and the Azulene Effect¹

Jack Saltiel*^{2a} and E. Dennis Megarity^{2b}

Contribution from the Department of Chemistry, Florida State University, Tallahassee, Florida 32306. Received September 24, 1971

Abstract: The azulene effect on *cis*–*trans* stationary states for direct stilbene photoisomerization is shown to be independent of solvent viscosity, while the azulene effect on the sensitized stilbene photoisomerization is shown to be viscosity dependent. The observations support the proposal that the azulene effect on the direct photoisomerization is due to long-range (~15 Å) radiationless excitation transfer from *trans*-stilbene singlets, whereas the azulene effect on the sensitized photoisomerization is due to diffusion-controlled excitation transfer from *trans*-stilbene triplets. Experiments in which Oil Yellow is used as the acceptor of stilbene excitation are similarly explained. It is concluded that intersystem crossing does not lie in the major path for direct stilbene photoisomerization. The unexpectedly large effect of azulene on the sensitized photoisomerization in *tert*-butyl alcohol is attributed to a ninefold increase of the effective lifetime of stilbene triplets in this solvent. The effect of azulene on the initial rates of benzophenone-sensitized *cis*-stilbene photoisomerization is found to be consistent with the proposed rapid conversion of *cis* triplets to *trans* triplets.

The studies of Dyck and McClure³ and Malkin and Fischer^{4,5} on the temperature dependence of the fluorescence quantum yield of *trans*-stilbene and *trans* → *cis* and *cis* → *trans* quantum yields of isomerization establish that almost all decay from the lowest excited singlet state of *trans*-stilbene, ¹t, can be accounted for by two processes: (1) fluorescence and (2) an activated crossing into the state from which isomerization takes place. Decay from *cis*oid excited singlets, ¹c, is practically temperature independent and leads almost exclusively to the state from which isomerization takes place. A marked drop in $\phi_{c \rightarrow t}$ at 77°K has been shown to be due mainly to increased medium rigidity and not to an internal barrier to rotation.^{5,6} Study of the direct *cis* → *trans* photoisomerization is complicated by the fact that a small fraction, $\lesssim 0.1$, of ¹c molecules undergoes cyclization to dihydrophenanthrene.^{7,8}

There has been much speculation concerning the identity of the state(s) involved in the *cis* → *trans* photoisomerization.⁹ Most recently, the major question has

concerned the identification of the activated process competing with *trans*-stilbene fluorescence. This process has been variously assigned to intersystem crossing into the triplet manifold (the triplet mechanism),^{4–6,10} or to twisting about the central bond of the lowest excited singlet state (the singlet mechanism).¹¹

Important in evaluating the triplet mechanism for stilbene photoisomerization have been studies involving the transfer of triplet excitation to the stilbenes from various triplets energy donors.^{5,12,13} Such studies yield quantitative information concerning the behavior of stilbene triplets and allow comparison of the triplets with the intermediates obtained upon direct excitation. Most informative in this respect have been experiments in which azulene is employed as an excitation acceptor in both the direct and the sensitized isomerization of the stilbenes.¹² Inclusion of azulene leads to stilbene photostationary states which are richer in *trans*-stilbene, but the effect is much larger for the sensitized photoisomerization. It has been suggested, on the basis of scintillation counting experiments, that the azulene effect on the direct photoisomerization is due entirely to radiationless transfer of excitation from *trans*-stilbene sing-

(1) A preliminary account of this work has been published: J. Saltiel and E. D. Megarity, *J. Amer. Chem. Soc.*, **91**, 1265 (1969).

(2) (a) Fellow of the Alfred P. Sloan Foundation; (b) National Institutes of Health Predoctoral Research Fellow, 1965–1969.

(3) R. H. Dyck and D. S. McClure, *J. Chem. Phys.*, **36**, 2326 (1962).

(4) S. Malkin and E. Fischer, *J. Phys. Chem.*, **66**, 2482 (1962).

(5) S. Malkin and E. Fischer, *ibid.*, **68**, 1153 (1964).

(6) D. Gegiou, K. A. Muszkat, and E. Fischer, *J. Amer. Chem. Soc.*, **90**, 12 (1968); S. Sharaby and K. A. Muszkat, *ibid.*, **93**, 4119 (1971).

(7) F. B. Mallory, C. S. Wood, and J. T. Gordon, *ibid.*, **86**, 3694 (1964).

(8) K. A. Muszkat and E. Fischer, *J. Chem. Soc. B*, 662 (1967).

(9) For a review of stilbene photoisomerization, see J. Saltiel, J. T.

D'Agostino, E. D. Megarity, L. Metts, K. R. Neuberger, M. Wrighton, and O. C. Zafiriou, *Org. Photochem.*, in press.

(10) Th. Förster, *Z. Electrochem.*, **56**, 716 (1952).

(11) J. Saltiel, *J. Amer. Chem. Soc.*, **89**, 1036 (1967); **90**, 6394 (1968).

(12) G. S. Hammond, J. Saltiel, A. A. Lamola, N. J. Turro, J. S. Bradshaw, D. O. Cowan, R. C. Counsell, V. Vogt, and C. Dalton, *ibid.*, **86**, 3197 (1964), and references cited therein.

(13) W. G. Herkstroeter and G. S. Hammond, *ibid.*, **88**, 4769 (1966).

lets to azulene and that the azulene effect obtained under triplet (sensitized) excitation conditions is due to excitation transfer from *trans*-stilbene triplets, 3t , to azulene.¹⁴ On this interpretation of the azulene effects rests the conclusion that intersystem crossing does not lie in the major path leading to direct *cis*-*trans* photoisomerization of the stilbenes. In the following, results are presented which strongly support the above interpretation of the azulene effects,¹⁴ and thus the singlet mechanism for stilbene photoisomerization.¹¹ Experiments are also described in which 2,3'-dimethyl-4'-aminoazobenzene (Oil Yellow) is used as the excitation energy acceptor.

Results

Sensitized Photoisomerization. A. Initial rates for the benzophenone-sensitized photoisomerization of *cis*-stilbene in benzene in the presence and in the absence of azulene are shown in Table I. Results of a

Table I. Azulene Effect on Initial Rates of Benzophenone-Sensitized *cis*-Stilbene Photoisomerization^a

<i>cis</i> -Stilbene, <i>M</i>	Benzophenone, <i>M</i>	Azulene, <i>M</i>	% <i>trans</i> -stilbene ^b
0.100	0.050	0	6.97 ± 0.05
0.100	0.050	0.010	8.12 ± 0.15
0.200	0.100	0.020	4.91 ± 0.11

^a Samples irradiated for the same time interval in the merry-go-round, filter no. 2 (see Experimental Section). ^b Corrected for back reaction: cf. A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, **43**, 2129 (1965).

control experiment carried out in order to determine whether azulene can sensitize *cis*-stilbene photoisomerization are shown in Table II. In a similar experiment

Table II. Azulene-Sensitization Control Experiment^a

<i>cis</i> -Stilbene, ^b <i>M</i>	Benzophenone, <i>M</i>	Azulene, <i>M</i>	Irradiation time, hr	% <i>trans</i> -stilbene
0.0100	0.050	0	2.00	55.4 ± 0.1 ^c
0.0100	0	0	2.00	1.29 ± 0.11
0.0100	0	0.200	2.00	~0.05
0.0100	0	0	6.75	4.00 ± 0.05
0.0100	0	0.200	6.75	~0.19

^a Samples were irradiated in parallel in benzene using the merry-go-round and filter no. 2. ^b Contained ~0.05% *trans* isomer. ^c Corrected for back reaction.

it was shown that irradiation of a benzene solution of Oil Yellow (0.01 *M*) in the presence of *cis*-stilbene (0.01 *M*) at 366 nm leads to no detectable stilbene isomerization.

B. Photostationary states for the sensitized isomerization of the stilbenes in the presence of azulene in *n*-pentane and *tert*-butyl alcohol, and the presence of Oil Yellow in benzene are shown in Table III.

Direct Excitation. A. Photostationary states for the direct isomerization of the stilbenes at 313 nm in the presence of azulene in benzene, *n*-pentane, and *tert*-butyl alcohol, and in the presence of Oil Yellow in benzene are shown in Table IV.

(14) J. Saltiel, E. D. Megarity, and K. G. Kneipp, *ibid.*, **88**, 2336 (1966).

Table III. Quencher Effects on Photostationary States of Sensitized Stilbene Isomerization^a

Solvent, sensitizer (<i>M</i>)	Quencher	Quencher concn, <i>M</i> × 10 ²	% [t] _h
<i>n</i> -Pentane, fluorenone (0.05 <i>M</i>)	Azulene	0	15.5 ± 0.1
		0.50	28.4 ± 0.5
		1.25	41.8 ± 0.3
		2.00	51.1 ± 0.2
<i>tert</i> -Butyl alcohol, benzophenone (0.02 <i>M</i>)	Azulene ^b	0	46.8 ± 0.2
		0.495	62.4 ± 0.1
		0.988	70.9 ± 0.2
		1.488	76.2 ± 0.2
		1.95	79.1 ± 0.4
Benzene, benzophenone (0.05 <i>M</i>)	Oil Yellow ^d	0	41.8 ± 0.4 ^c
		0.50	48.1 ± 0.1
		0.100	53.1 ± 0.1

^a Filter no. 1. ^b Azulene concentrations determined by uv analysis following irradiation. ^c From ref 11. ^d Some *trans* → *cis* isomerization of Oil Yellow may have occurred; see Experimental Section.

Table IV. Quencher Effects on Photostationary States by Direct Stilbene Isomerization^a

Solvent, quencher	Quencher concn, (<i>M</i> × 10 ²)	% [t] _h
Benzene, azulene	0	10.44 ± 0.1
	0.200	10.6 ± 0.1
	0.400	11.0 ± 0.1
	0.800	11.5 ± 0.1
	1.200	11.95 ± 0.15
	2.00	12.9 ± 0.1
Benzene, azulene ^b	0	10.05 ± 0.1
	0.200	10.45 ± 0.1
	0.400	10.5 ± 0.1
	0.800	11.2 ± 0.2
	1.200	11.8 ± 0.1
	2.00	12.95 ± 0.15
<i>n</i> -Pentane, azulene	0.100	8.5 ± 0.1
	0.500	8.7 ± 0.2
	1.25	9.5 ± 0.2
	1.60	10.1 ± 0.2
	2.00	10.4 ± 0.1
	<i>tert</i> -Butyl alcohol, azulene ^c	0.255
1.08		12.9 ± 0.1
1.56		13.8 ± 0.2
2.11		14.5 ± 0.3
2.53		14.9 ± 0.2
Benzene, Oil Yellow		0
	0.500	17.9 ± 0.5
	1.50	24.5 ± 0.3
	2.50	36.5 ± 0.5

^a Filter no. 3 unless otherwise indicated. ^b Filter no. 4. ^c Azulene concentrations in irradiated samples determined by uv analysis.

B. Relative fluorescence quantum yields of *trans*-stilbene in *n*-pentane, benzene, and *tert*-butyl alcohol were determined at 24° using 305 nm as the excitation wavelength. Stilbene concentrations (~3 × 10⁻⁵ *M*) were adjusted so that all solutions had the same absorbance at 305 nm. Relative ϕ_F values, corrected for differences in index of refraction,¹⁵ are given in Table V.

Discussion

The relative energies of the 0S , 1S , and 1T states of the stilbenes and of the sensitizers and quenchers used in

(15) A. Testa, *Fluorescence News*, **4**, 1 (1969).

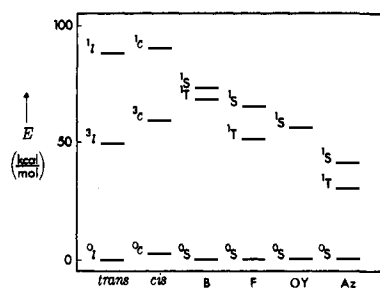


Figure 1. Lowest energy electronic states for the stilbenes, the sensitizers, and the quenchers used in this study: B = benzophenone, F = fluorenone, OY = Oil Yellow, Az = azulene.

this study are shown in Figure 1. In the figure, as well as throughout this discussion, ${}^0t, {}^0c, {}^1t, {}^1c,$ and ${}^3t, {}^3c$ represent the ${}^0S, {}^1S,$ and 1T electronic states of near-planar *trans*- and *cis*-stilbene, respectively. The ground state energy difference between the two isomers has been

Table V. Relative Fluorescence Quantum Yields of *trans*-Stilbene

Solvent	n_{20}° ^a	Relative ϕ_F
Benzene	1.5011	1.00 ^b
<i>n</i> -Pentane	1.3575	0.97
<i>tert</i> -Butyl alcohol	1.3878	0.72

^a N. A. Lange, Ed., "Handbook of Chemistry," 9th ed, Handbook Publishers, Sandusky, Ohio, 1956, pp 1282, 1285, 1348. ^b Assumed.

assumed to be equal to the enthalpy difference of 2.3 kcal/mol obtained from the temperature dependence of the thermodynamic equilibrium constant in toluene.¹⁶ Singlet excitation energies for the stilbenes refer to the 0-0 bands of the fluorescence and absorption spectra of the *trans* isomer, and the 0-0 band in the absorption spectrum of the *cis* isomer, all measured at 20°K.³ The large Stokes red shift (~ 4.5 kcal/mol) which is exhibited by the weak fluorescence of *cis*-stilbene in a rigid medium at 77°K¹⁷⁻¹⁹ indicates that the energy given for 1c should be regarded as an upper limit. Since phosphorescence has not been detected from the stilbenes, the triplet excitation energies are based on weak ${}^1T \leftarrow {}^0S$ absorption spectra which have been measured in the presence of high oxygen pressures^{20,21} and in ethyl iodide.^{3,22} The excitation energies for the lowest singlet and triplet states of benzophenone and fluorenone are taken from ref 23 and 24, respectively. The azulene excitation energies are based on its absorption spectrum²⁵ and the weak emission spectra which have been recently reported.²⁶ The en-

(16) G. Fischer, K. A. Muszkat, and E. Fischer, *J. Chem. Soc. B*, 156 (1968).

(17) H. Stegemeyer and H. H. Perkampus, *Z. Phys. Chem. (Frankfurt am Main)*, **39**, 125 (1963).

(18) F. Aurich, M. Hauser, E. Lippert, and H. Stegemeyer, *ibid.*, **42**, 123 (1964).

(19) A. A. Lamola, G. S. Hammond, and F. B. Mallory, *Photochem. Photobiol.*, **4**, 259 (1965).

(20) D. F. Evans, *J. Chem. Soc.*, 1351 (1957).

(21) A. Bylina and Z. R. Garbowski, *Trans. Faraday Soc.*, **65**, 458 (1969).

(22) H. Stegemeyer, *Z. Phys. Chem. (Frankfurt am Main)*, **51**, 95 (1966).

(23) J. Saltiel, H. C. Curtis, L. Metts, J. W. Miley, J. Winterle, and M. Wrighton, *J. Amer. Chem. Soc.*, **92**, 410 (1970).

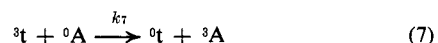
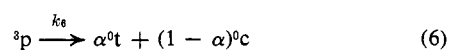
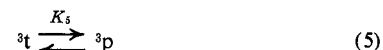
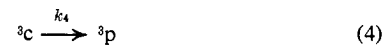
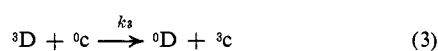
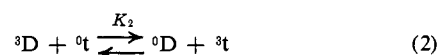
(24) K. Yoshihara and D. R. Kearns, *J. Chem. Phys.*, **45**, 1991 (1966), and references cited therein.

(25) E. Clar, *J. Chem. Soc.*, 1823 (1950).

(26) P. M. Rentzepis, *Chem. Phys. Lett.*, **3**, 717 (1969).

ergy of the lowest excited singlet state of Oil Yellow was estimated from its absorption spectrum. The location of the lowest triplet state of Oil Yellow is unknown, but since the rates of triplet excitation transfer from acetylpyrene ($E_T = 45$ kcal/mol) to *cis*- and *trans*-azobenzenes appear to be diffusion controlled,^{27,28} it is not likely to be higher than 40 kcal/mol.

Triplet State Azulene Effect. The simplest mechanism which accounts for most observations involving the sensitized photoisomerization of the stilbenes is shown in eq 1-7, where D stands for the donor, A for



any acceptor whose triplet excitation energy is sufficiently low to preclude its functioning as a donor for the stilbenes, *i.e.*, $k_{-7} = 0$, p designates a twisted vibrationally relaxed conformation of stilbene, and α is the fraction of twisted triplets decaying to 0t .¹¹⁻¹³ Using the steady-state assumption and assuming rapid equilibration of 3t and 3p , *i.e.*, $k_5 \gg k_7[A]$, eq 8 is obtained for

$$\left(\frac{[t]}{[c]}\right)_s = \left(\frac{k_3}{k_2}\right) \left(\frac{\alpha}{1 - \alpha} + \frac{k_{-2}[D] + k_7[A]}{(1 - \alpha)k_6K_5}\right) \quad (8)$$

the $[t]/[c]$ ratio at photoequilibrium, where subscripts indicates the stationary state condition.¹¹ For the donors used in this study, excitation transfer to 0t has been shown to be irreversible at room temperature, *i.e.*, $k_{-2} = 0$.^{12,13} Since the ${}^0c \rightarrow {}^3p$ process most likely corresponds to the Franck-Condon forbidden 0-0 band of the ${}^0S \rightarrow {}^1T$ transition of *cis*-stilbene, its representation in the mechanism in two steps may be meaningful only in highly viscous media.^{6,9,29,30}

Azulene and Oil Yellow meet the energetic criterion for functioning as efficient acceptors of triplet excitation from 3t , Figure 1. In the case of azulene, reaction 7 is at least 15 kcal/mol exothermic and is therefore expected to be diffusion controlled.³¹ Plots of $([t]/[c])_s$ against quencher concentration are linear, Figure 2, as previously reported,^{11,12} in accord with eq 8. The difference in intercepts in Figure 2 for the benzophenone-sensitized photoisomerizations in benzene and *tert*-butyl alcohol is assumed to reflect a small solvent dependence in the decay ratio, $\alpha/(1 - \alpha)$. This assumption is based on observations which suggest that the benzophenone excitation ratio, k_3/k_2 , in benzene is unity with excitation transfer to either isomer being

(27) L. B. Jones and G. S. Hammond, *J. Amer. Chem. Soc.*, **87**, 4219 (1965).

(28) *Cf.* also, E. Fischer, *ibid.*, **90**, 796 (1968).

(29) G. S. Hammond and J. Saltiel, *ibid.*, **85**, 2516 (1963).

(30) A. Bylina, *Chem. Phys. Lett.*, **1**, 509 (1968).

(31) Diffusion-controlled triplet excitation transfer from anthracene ($E_T = 42$ kcal/mol) to azulene has been reported.^{32,33}

(32) W. Ware, *J. Chem. Phys.*, **37**, 923 (1962).

(33) A. A. Lamola, W. G. Herkstroeter, J. C. Dalton, and G. S. Hammond, *ibid.*, **42**, 1715 (1965).

diffusion controlled.¹³ The observation of diffusion-controlled excitation transfer in benzene practically assures diffusion-controlled excitation transfer in the more viscous solvent *tert*-butyl alcohol.³⁴ The difference in intercepts between the lines for the benzophenone-sensitized isomerization in benzene and the fluorenone-sensitized isomerization in *n*-pentane is due to fluorenone's smaller than unity excitation ratio, $k_3/k_2 = 0.26$.¹¹⁻¹³ The identity of 3p decay ratios in benzene and *n*-pentane is inferred from the identical photo-stationary state ratios obtained with fluorenone as the triplet energy donor in the two solvents.^{11,12} Fluorenone was chosen for the *n*-pentane experiments because the π, π^* character and lower energy of its lowest triplet state²⁴ suggest that it would be less susceptible to photoreduction.

The values of k_7/k_6K_5 , obtained from the slope/intercept ratios in Figure 2 and the appropriate value of α , are shown in Table VI. If excitation transfer to

Table VI. Azulene Effect on the Sensitized Stilbene Photoisomerization at 30°

Solvent	η , cP ^a	α	k_7/k_6K_5 , M ⁻¹	
			Obsd	Calcd
<i>n</i> -Pentane	0.220	0.415	97	135
Benzene ^b	0.561	0.415	53	53 ^c
Benzene			23 ^d	
<i>tert</i> -Butyl alcohol	3.316	0.478	79	9 (82) ^e

^a *n*-Pentane and benzene, see footnote a, Table V, pp 1658, 1660; *tert*-butyl alcohol, J. Timmermans, "Physico-Chemical Constants of Pure Organic Compounds," Elsevier, New York, N. Y., 1950, p 325. ^b Reference 11. ^c Assumed. ^d Oil Yellow quencher. ^e See text.

azulene, eq 7, occurred upon every encounter in each of the solvents studied and if k_7 were the only solvent-dependent constant in the ratio, the magnitude of k_7/k_6K_5 would be proportional to η^{-1} as predicted by the Debye equation for a diffusion-controlled process.³⁴ The calculated values of k_7/k_6K_5 in Table VI are based on this assumption. The agreement between the calculated and observed ratios in changing the solvent from benzene to *n*-pentane is satisfactory, although the value in *n*-pentane is somewhat smaller than expected. It appears that either k_7 is not entirely diffusion controlled in *n*-pentane, or that k_6 and/or K_5 are also solvent dependent. Precedent for the first possibility is available in observations which indicate that exothermic triplet excitation transfers can be less than completely diffusion controlled in the most fluid solvents.³⁴ The most striking deviation from the predicted behavior is observed in the case of *tert*-butyl alcohol. Since k_7 must surely be diffusion controlled in so viscous a solvent,³⁴ the result suggests a marked increase in the effective lifetime of stilbene triplets, $1/k_6K_5$, in alcoholic solvents. Data reported by Liu with 9,10-dichloroanthracene, DCA, as the acceptor in eq 7 strongly support this conclusion.³⁵ The effect of DCA on the sensitized photoisomerization of the stilbenes obeys eq 8 and gives k_7'/k_6K_5 values of 71 and 206 in benzene and *n*-propyl alcohol, respectively.³⁵ On the basis of these results the Debye equation predicts $k_7/k_6K_5 = 82$ for azulene as the acceptor in *tert*-

(34) P. J. Wagner and I. Kochevar, *J. Amer. Chem. Soc.*, **90**, 2232 (1968).

(35) R. S. H. Liu, *ibid.*, **90**, 1899 (1968).

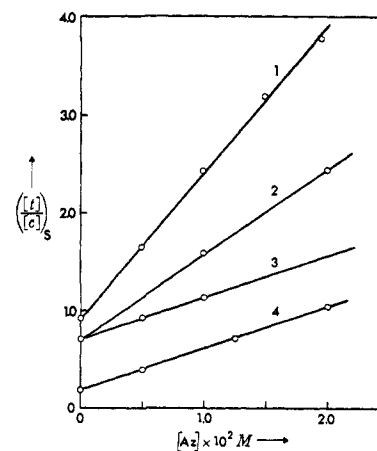
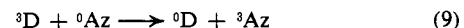


Figure 2. The effect of quencher on sensitized-stilbene photo-stationary ratios. Sensitizer, quencher, and solvent are as follows: line 1, benzophenone, azulene, and *tert*-butyl alcohol; line 2,¹¹ benzophenone, azulene, and benzene; line 3, benzophenone, Oil Yellow, and benzene; line 4, fluorenone, azulene, and *n*-pentane.

butyl alcohol. This value, shown in parentheses in Table VI, is in excellent agreement with the observed value. It appears, therefore, that the effective lifetime of stilbene triplets increases ninefold on changing from hydrocarbon to alcoholic solvents, $\sim 10^{-8}$ and $\sim 10^{-7}$ sec, respectively.⁹ It can be further concluded that within either set of solvents the Debye equation is obeyed quite well.³⁶ It is not presently known whether the lifetime increase in alcohols should be attributed to k_6 , K_5 , or to both constants. However, an attractive possibility is that it reflects a decrease in K_5 as the viscosity of the solvent is increased. This would result in the storing of more stilbene triplet in the transoid conformation, 3t , from which intersystem crossing to the ground state has been shown to be negligible under the conditions of the above experiments.^{11,37}

In the above discussion of stilbene triplet decay, a rapid equilibration between 3p and 3t has been assumed. Compelling evidence favoring $^3p \rightarrow ^3t$ conversion has not yet been discussed. The experiments considered thus far could also be explained by assuming an activated irreversible conversion of 3t to a more stable 3p .³⁸ Effective stilbene triplet lifetimes would then equal $1/k_6$, and a viscosity effect on the lifetime of 3t could be attributed to an additional solvent imposed barrier to twisting about the central bond in the more viscous solvents.^{37,39} If this mechanism were correct, excitation to 3c would not lead to formation of 3t triplets. This prediction was tested by measuring the azulene effect on initial rates of the benzophenone-sensitized isomerization of *cis*-stilbene, Table I. Since azulene is an efficient excitation acceptor from benzophenone triplets,^{33,41} eq 9 must be included in either mechanistic description of



(36) R. S. H. Liu has informed us that his unpublished observations with DCA support this conclusion.

(37) W. G. Herkstroeter and D. S. McClure, *J. Amer. Chem. Soc.*, **90**, 4522 (1968).

(38) We thank Professor E. Fischer for suggesting this possibility to us.

(39) This would be analogous to the viscosity effect on the singlet path to stilbene photoisomerization.^{11,40}

(40) J. Saltiel and J. T. D'Agostino, manuscript in preparation.

(41) G. S. Hammond and P. A. Leermakers, *J. Phys. Chem.*, **66**, 1148 (1962).

the benzophenone-*cis*-stilbene-azulene system. In addition, partial absorption by azulene of the incident radiation, 366 nm, must be accounted for. Expressions for the *cis* → *trans* quantum yield in the presence of azulene for $k_5 \gg k_{-6}$ and $k_{-5} = 0$ are given in eq 10

$$\phi_{c \rightarrow t} = \left(\frac{\epsilon_D [^0D]}{\epsilon_D [^0D] + \epsilon_{Az} [^0Az]} \right) \left(\frac{k_3 [^0c]}{k_3 [^0c] + k_9 [^0Az]} \right) \times \left(\frac{\alpha k_6 K_5 + k_7 [^0Az]}{k_6 K_5 + k_7 [^0Az]} \right) \quad (10)$$

and 11, respectively, where ϵ_D and ϵ_{Az} are the molar

$$\phi_{c \rightarrow t} = \left(\frac{\epsilon_D [^0D]}{\epsilon_D [^0D] + \epsilon_{Az} [^0Az]} \right) \left(\frac{k_3 [^0c]}{k_3 [^0c] + k_9 [^0Az]} \right) \alpha \quad (11)$$

extinction coefficients of benzophenone and azulene in benzene at 366 nm, 67 and 23.7 $M^{-1} \text{ cm}^{-1}$, respectively. In eq 10 and 11 the first term represents the fraction of light absorbed by the donor leading, in this case, to triplets with unit efficiency, the second term represents the fraction of donor triplets which transfer excitation to *cis*-stilbene, and the third term represents the fraction of stilbene triplets which decay to *trans*-stilbene. The ratio of the rate constants of triplet excitation transfer from benzophenone to azulene and *cis*-stilbene, k_9/k_3 , is not known, but can be assumed to be similar to the corresponding ratio of 1.47 for excitation transfer from benzophenone to azulene and naphthalene.⁴¹ Comparison of the observed quantum yields with those calculated using eq 10 and 11, Table VII, shows that only eq 10 satisfactorily accounts for

Table VII. Azulene Effect on Benzophenone-Sensitized *cis*-Stilbene Photoisomerization

Concn, M			Obsd	Calcd, eq 10 ^b	Calcd, eq 11 ^b
⁰ c	⁰ D	⁰ Az			
0.100	0.050	0	0.41 ^a	0.41	0.41
0.100	0.050	0.010	0.48	0.50	0.34
0.200	0.100	0.020	0.58	0.61	0.34

^a Assumed equal to α ; the observed value is 0.42 ± 0.03 (H. A. Hammond, D. E. DeMeyer, and J. L. R. Williams, *J. Amer. Chem. Soc.*, **91**, 5180 (1969)). ^b Using $\epsilon_D = 67 M^{-1} \text{ cm}^{-1}$, $\epsilon_{Az} = 23.7 M^{-1} \text{ cm}^{-1}$, $k_9/k_3 = 1.47$, $\alpha = 0.415$, and $k_7/k_6 K_5 = 53 M^{-1}$.

the observations in Table I. The assumption that the $^3c \rightarrow ^3p \rightleftharpoons ^3t$ conversions take place is thus confirmed. It is noted here that irradiation of azulene alone in the presence of *cis*-stilbene does not lead to *cis* → *trans* isomerization, Table II. The conversion of 3c to 3t has been further confirmed by observations concerning decay from donor-acceptor encounter cages involving low triplet energy donors.⁴²

Test of the Triplet Mechanism for Direct Photoisomerization. A mechanism which could in principle account for the azulene effect on photostationary states obtained upon direct excitation of the stilbenes is given by eq 12-17 and 4-7. In addition to triplet



(42) M. Wrighton, L. Metts, and J. Saltiel, presented at the Joint Conference of the Chemical Institute of Canada and the American Chemical Society, Toronto, Canada, 1970, Abstract ORGN-048.



excitation transfer, eq 7, the transfer of singlet excitation from *trans* singlets, 1t , to azulene, eq 17, is energetically feasible, Figure 1. Energy transfer from 1c to azulene is neglected because the lifetime of 1c is expected to be very short in nonviscous media.^{6,17-19,43,44} The mechanism yields stationary-state relationship 18 where ϵ_c

$$\left(\frac{[t]}{[c]} \right)_s = \left(\frac{\epsilon_c}{\epsilon_t} \right) \left(\frac{k_{14} + k_{16} + k_{17}[A]}{k_{14}} \right) \times \left(\frac{\alpha}{1 - \alpha} + \frac{k_7[A]}{k_6 K_5 (1 - \alpha)} \right) \quad (18)$$

and ϵ_t are extinction coefficients of *cis*- and *trans*-stilbene at the exciting wavelength. The minimum azulene effect predicted by eq 18 would be observed if singlet excitation transfer were negligible, *i.e.*, $(k_{14} + k_{16}) \gg k_{17}[A]$. Subject to this condition $([t]/[c])_s$ ratios would be expected to vary linearly with azulene concentration with slope/intercept ratios equal to $k_7/\alpha k_6 K_5$. Thus, the triplet mechanism for the direct photoisomerization predicts that the minimum azulene effect would give slope to intercept ratios which are identical with those obtained for the sensitized photoisomerization, Figure 2. If singlet excitation transfer were also operative $([t]/[c])_s$ ratios for the direct photoisomerization would be more sensitive to added azulene than for the sensitized photoisomerization and plots of $([t]/[c])_s$ vs. $[Az]$ would be curved. Analysis of the data in Table IV shows that $([t]/[c])_s$ ratios increase linearly with azulene concentration but that the observed effects of azulene are much smaller than the minimum effects predicted by eq 18. Slope/intercept ratios for the direct and sensitized isomerization are shown in Table VIII. Also included in Table VIII are

Table VIII. Comparison of Azulene Effects on Direct and Sensitized Isomerization of the Stilbenes

Solvent	Slope/intercept ^a	
	Direct ^b	Sensitized
<i>n</i> -Pentane	14.2	237
Benzene	14.0, 16.5 ^c , 22 ^d	130 ^e
Benzene ^f	152	57
<i>tert</i> -Butyl alcohol	16.1	164

^a Least-squares analysis. Data from this work gave linear correlation coefficients >0.99 in all cases. ^b Using filter no. 3 unless otherwise indicated. ^c Filter no. 4. ^d Reference 12, a different filter system and lower stilbene concentration were used in this study. ^e Reference 11. ^f Oil Yellow quencher.

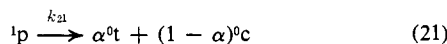
results (to be discussed below) from observations with Oil Yellow as quencher. Calculated (eq 18) and observed variations of photostationary ratios with azulene concentration in *n*-pentane are shown in Figure 3. It is concluded that the failure of eq 18 in predicting the

(43) G. N. Lewis, T. T. Magel, and D. Lipkin, *J. Amer. Chem. Soc.*, **62**, 2973 (1940).

(44) D. Schulte-Frohlinde, H. Blume, and H. Gusten, *J. Phys. Chem.*, **66**, 2486 (1962).

very small observed effects provides a firm basis for the rejection of the triplet mechanism for the direct photoisomerization of unperturbed stilbenes. A crucial feature of the data in Table VIII is that, whereas the azulene effect on the sensitized photoisomerization is sensitive to changes in solvent viscosity, the effect of azulene on the direct photoisomerization is independent of solvent viscosity. Were the formation of triplet states responsible for a significant fraction (>5%) of the azulene effect on the direct photoisomerization, some dependence of slope/intercept ratios on viscosity would have been observed. This assertion is supported by observations with *p*-bromostilbene for which the triplet mechanism provides the minor path (~30%) for the direct isomerization at 30°. ⁴⁵

Azulene Effect on the Direct Photoisomerization. Having rejected the triplet mechanism for the direct photoisomerization of the stilbenes, the effect of azulene under these conditions can be explained by assuming singlet excitation transfer from ¹t, eq 17, using the singlet mechanism for the photoisomerization, eq 12, 13, 16, and 19–21. ¹¹ This mechanism leads to photostationary



expression 22 thus predicting the observed linear

$$\left(\frac{[t]}{[c]}\right)_s = \left(\frac{\epsilon_c}{\epsilon_t}\right) \left(\frac{\alpha}{1 - \alpha}\right) \left(\frac{k_{16} + k_{19}}{k_{19}} + \frac{k_{17}[A]}{k_{19}}\right) \quad (22)$$

relationship between $([t]/[c])_s$ and azulene concentration. The rate constant of ¹t fluorescence, $k_{16} = 4 \times 10^8 \text{ sec}^{-1}$, has been calculated from the integrated absorption of the ¹S ← ⁰S transition in *trans*-stilbene. ³ Using the fluorescence quantum yield of *trans*-stilbene in methylcyclohexane at 26°, $\phi_F = 0.046$, ^{6,40} an approximate value of the actual lifetime of ¹t in the absence of azulene, $(k_{16} + k_{19})^{-1} \approx 1.2 \times 10^{-10} \text{ sec}$, can be calculated, where k_{19} represents the rate constant for twisting about the central bond (*i.e.*, for the activated process which leads to isomerization). The insensitivity of the direct excitation azulene effect to changes in solvent viscosity can now be readily explained since, in order to compete with first-order decay from ¹t, singlet excitation transfer, eq 17, must occur over distances greater than normal collisional diameters. ⁴⁶

The values of α shown in Table IX are obtained from the intercepts of the azulene plots using eq 23 which is

$$\alpha = (1 + [(1 - \phi_F)(\epsilon_t/\epsilon_c)([t]/[c])_s]^{-1})^{-1} \quad (23)$$

derived from eq 22. Comparison with the α values in Table VI confirms the earlier conclusion that the decay characteristics of ¹p and ³p are very similar. ^{11,47} It should be noted at this point that eq 22 and 23 may not be exact because in deriving them the reversible formation of dihydrophenanthrene (DHP), eq 24 and 25, has



(45) J. Saltiel and E. D. Megarity, manuscript in preparation.

(46) R. G. Bennett and R. E. Kellogg, *Progr. React. Kinet.*, **4**, 215 (1967).

(47) G. S. Hammond and J. Saltiel, *J. Amer. Chem. Soc.*, **84**, 4983 (1962).

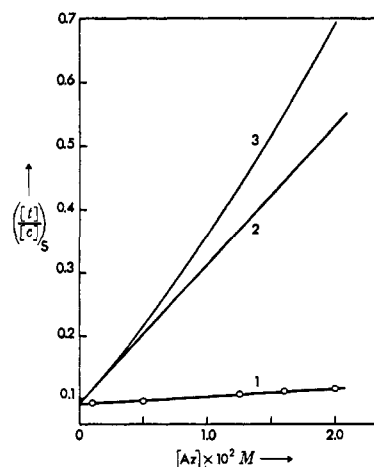


Figure 3. Azulene effect on the direct photoisomerization of the stilbenes in *n*-pentane: line 1, experimentally observed; line 2, calculated using eq 18 assuming $k_{17} = 0$; line 3, calculated using eq 18 assuming $k_{17}/(k_{14} + k_{16}) = 14 \text{ M}^{-1}$.

been neglected. ^{7,8} However, this omission is probably not serious since steady-state concentrations of DHP were minimized by simultaneous irradiation in the visible region where DHP exhibits strong absorption. ⁸ Furthermore, a set of experiments in benzene which differ only in that visible light has been excluded, Tables IV and VIII, shows that the presence of visibly higher concentrations of DHP does not significantly alter $([t]/[c])_s$ ratios.

Table IX. Rate Constants for the Direct Photoisomerization

Solvent	ϕ_F^a	α^b	$k_{17}^c \times 10^{-11}, \text{ M}^{-1} \text{ sec}^{-1}$	$k_{19}^c \times 10^{-10}, \text{ sec}^{-1}$
<i>n</i> -Pentane	0.046	0.40	1.2	0.8
Benzene	0.048	0.44	1.2	0.8
<i>tert</i> -Butyl alcohol	0.035	0.48	1.9	1.1

^a From Table V assuming $\phi_F = 0.046$ for *n*-pentane. ⁴⁰ ^b Using eq 23. ^c Assuming $k_{16} = 4 \times 10^8 \text{ sec}^{-1}$ throughout.

According to eq 22, slope/intercept ratios for the direct photoisomerization, Table VIII, are equal to $k_{17}/(k_{16} + k_{19})$. Values for k_{17} and k_{19} , Table IX, are obtained from these ratios and the fluorescence quantum yields of *trans*-stilbene by assuming that ϕ_F in *n*-pentane equals ϕ_F in methylcyclohexane, and that the rate of radiative decay from ¹t, k_{16} , is not solvent dependent. The latter assumption is supported by the fact that ¹S ← ⁰S absorption spectra of *trans*-stilbene at room temperature show little sensitivity to solvent changes (see Experimental Section and ref 3). ⁴⁸ The rate constants for singlet excitation transfer, k_{17} , do not decrease as the solvent viscosity is increased and are significantly larger than the rate constant for a diffusion-controlled process in each solvent. The higher viscosity of *tert*-butyl alcohol was expected to hinder the twisting process, eq 19, giving rise to a somewhat higher fluorescence yield. ⁴⁰ Since the observed fluorescence yield is relatively low, it

(48) Actually the rate constant for a radiative transition is expected to be proportional to $9n/(n^2 + 1)^2$ where n is the index of refraction of the medium. ⁴⁹ For the solvents used, variations due to index of refraction corrections amount to $\leq 11\%$ of k_{16} and are neglected.

(49) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," Wiley, New York, N. Y., 1966, p 172.

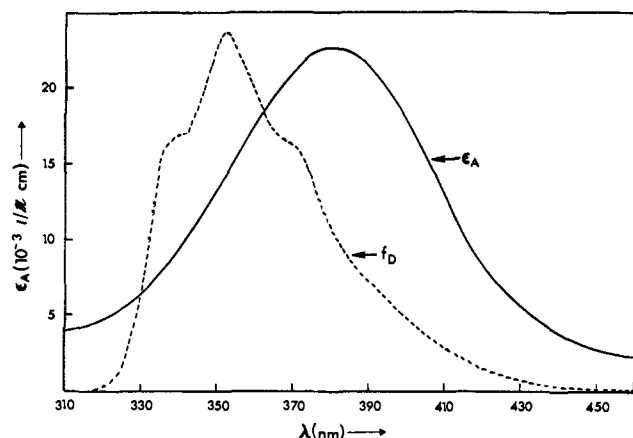


Figure 4. Spectral overlap between *trans*-stilbene fluorescence and Oil Yellow absorption.

may be in error, and no great significance is attached to the small apparent increase in k_{17} and k_{19} in this solvent.

Theoretical expressions describing long-range singlet energy transfer have been derived by Förster.⁴⁶ For the case of weak coupling, R_0 , the distance in centimeters at which the transfer rate equals the normal decay rate of the excited donor, is given by eq 26 where ϕ_D is the

$$R_0 = \left(\frac{(8.79 \times 10^{-25}) K^2 \phi_D}{n^4} \int_0^\infty f_D(\bar{\nu}) \epsilon_A(\bar{\nu}) \frac{d\bar{\nu}}{\bar{\nu}^4} \right)^{1/6} \quad (26)$$

fluorescence quantum yield of the donor, K^2 is an orientation factor (taken as $2/3$ for random distribution), n is the index of refraction of the solvent, f_D is the donor fluorescence spectrum normalized to unity, and ϵ_A is the acceptor molar decadic extinction coefficient. The integral in eq 26 is large when there is good spectral overlap between donor fluorescence and acceptor absorption. The spectral overlap between *trans*-stilbene fluorescence and azulene absorption in benzene, shown in Figure 1 of ref 1, gives rise to a calculated value of R_0 of 15 Å.^{50,51} The experimental value of R_0 in ångströms is given approximately by eq 27.^{1,52} Substitution of the

$$R_0 = 6.32 \left(\frac{k_{17}}{k_{16} + k_{19}} \right)^{1/3} \quad (27)$$

rate constant ratio from Table IX in eq 27 gives 15 Å for the value of R_0 in benzene, in excellent agreement with the theoretical value. Derivation of eq 26 is based on the assumption that R_0 is large compared to molecular dimensions. The exact correspondence between the theoretical and experimental values of R_0 is interesting since this assumption is marginal in this case.⁵³ It is concluded that the above observations establish definitively that the azulene effect on the direct photoisomerization is completely accounted for by eq 17.

The observations with Oil Yellow show that the functioning of azulene as a singlet excitation acceptor from 1t is not unique. Its use instead of azulene produces larger changes in direct isomerization photostationary states than in benzophenone-sensitized photostationary states, Table VIII. This reversal in the magnitude of

the quencher effects can be partially attributed to the much stronger overlap between the fluorescence of *trans*-stilbene and the absorption spectrum of Oil Yellow (compare Figure 4 with Figure 1 in ref 1). It is also due to a somewhat lower rate constant for triplet excitation transfer, k_7 , from 3t to Oil Yellow. The theoretical and experimental R_0 values for singlet excitation transfer to Oil Yellow are 23 and 34 Å, respectively. The agreement is not as good as for the case of azulene, but agreement to within 40% of the experimental value has been considered acceptable⁵⁴ and whenever theoretical and experimental values differ, the latter are usually found to be the larger of the two.⁵⁴

Conclusion

The triplet mechanism for direct stilbene photoisomerization fails to account for observations concerning the transfer of electronic excitation to azulene, whereas the singlet mechanism accounts for these observations very satisfactorily. It is concluded, therefore, that intersystem crossing is not an important decay path for unperturbed stilbene at ambient temperature. Observations concerning the stilbenes and glycerol are readily interpreted by the singlet mechanism.^{6,40} External and internal heavy atom effects, or substituents which generally enhance intersystem crossing efficiency, may alter the mechanism for the photoisomerization so that triplet states may become involved,^{9,45,55} but in each case more study is required in order to determine the extent of triplet involvement. It is of considerable interest that differential azulene quenching experiments of direct and sensitized photoisomerization of two bis-pyridylethylenes have led to the conclusion that the direct *cis* \rightarrow *trans* photoisomerization bypasses the triplet state in these systems as well.⁵⁶

Experimental Section

Materials. *trans*-Stilbene, K & K scintillation grade, was recrystallized from ethanol and sublimed. It was shown by glpc to contain less than 0.3% of the *cis* isomer. *cis*-Stilbene was either Aldrich research grade, distilled on an 18-in. Nester/Faust spinning-band column, or was obtained by the pyrene-sensitized photoisomerization of the *trans* isomer.¹¹ *cis*-Stilbene obtained from the *trans* isomer was isolated by alumina chromatography and vacuum distilled. Glpc analysis showed that neither sample of *cis*-stilbene contained more than 0.2% of the *trans* isomer, but the purified Aldrich sample contained a trace of β -methyl-naphthalene (<0.4%). Benzophenone, Fischer reagent grade, was recrystallized from pentane and sublimed. Fluorenone, K & K reagent grade, was purified by alumina chromatography followed by recrystallization from cyclohexane. Azulene, Baker reagent grade, was sublimed twice. Oil Yellow powder dye, generously supplied by Dr. R. G. Bennett of DuPont, was purified by alumina chromatography. Benzene, Baker reagent grade, was purified by the Steinmetz procedure as previously described, purity >99.999% by glpc.¹¹ *n*-Pentane, Matheson Coleman and Bell spectroquality, was passed through alumina and fractionally distilled using a 13 mm o.d. \times 4 ft vacuum jacketed column filled with Helipac packing, Podbielniac Corp. This column was used for the final distillation of all solvents. *tert*-Butyl alcohol, Matheson Coleman and Bell reagent grade, was fractionally distilled.

Analytical Procedures. Ketone sensitizers, when present, were removed by alumina chromatography. Stilbene samples were concentrated on a hotplate under a stream of nitrogen. This treatment was shown not to affect *trans/cis* ratios provided com-

(50) The previous value¹ of 16 Å was based on $\phi_F = 0.08$,⁴ rather than 0.048.

(51) We thank Dr. A. A. Lamola for the evaluation of the integral in eq 26.

(52) R. Povinelli, Ph.D. Thesis, University of Notre Dame, 1964.

(53) D. W. Ellis and B. S. Solomon, *J. Chem. Phys.*, **46**, 3497 (1967).

(54) Cf., for example, W. R. Ware, *J. Amer. Chem. Soc.*, **83**, 4374 (1961).

(55) D. Gegiou, K. A. Muszkat, and E. Fischer, *ibid.*, **90**, 3907 (1968).

(56) Y. J. Lee, D. G. Whitten, and L. Pedersen, *ibid.*, **93**, 6330 (1971). We thank Dr. Whitten for sending us a copy of this manuscript prior to publication.

plete evaporation of the solvent was avoided (otherwise *cis*-stilbene is lost preferentially). Stilbene compositions were determined by glpc (3 ft \times 1/8 in. column of 5% Apiezon M on Chromosorb W, \sim 170°) using an Aerograph Model 600 C Hy-Fi gas chromatograph with recalibrated attenuator circuit resistors.⁵⁷ The recorder was a Leeds-Northrup Speedomax W equipped with a Disc integrator. In the case of *tert*-butyl alcohol, azulene concentrations were checked following irradiation, by measuring the absorbance at 577.5 nm. This was necessary because in some samples, for unknown reasons, the azulene was partially consumed during the course of the irradiation. In the case of the benzophenone-sensitized photoisomerization in the presence of Oil Yellow (0.01 *M*), no loss of Oil Yellow was detected by glpc, although there was a 20% decrease in the absorbance of the solution at 380 nm. This decrease may be due to *trans* \rightarrow *cis* photoisomerization of Oil Yellow.^{27,28}

Absorption Spectra. Ultraviolet and visible absorption spectra were recorded at room temperature using Cary-14 or -15 spectrophotometers. Spectral features of the ¹S \leftarrow ⁰S transition in *trans*-stilbene are: benzene, shoulder at 324.0 nm (ϵ 2.67 \times 10⁴), maxima at 310.5 (ϵ 2.64 \times 10⁴) and 298.5 nm (ϵ 2.67 \times 10⁴); *n*-pentane, shoulder at 320.0 nm (ϵ 1.42 \times 10⁴), maxima at 306.0 (ϵ 2.45 \times 10⁴) and 292.0 (ϵ 2.80 \times 10⁴); *tert*-butyl alcohol, shoulder at 320.0 nm (ϵ 1.57 \times 10⁴), maxima at 306.3 (ϵ 2.5 \times 10⁴) and 294.0 nm (ϵ 2.75 \times 10⁴). Extinction coefficients at 313.0 nm for *trans*- and *cis*-stilbene, respectively, are: benzene, 2.58 \times 10⁴, 0.354 \times 10⁴; *n*-pentane, 1.862 \times 10⁴, 0.238 \times 10⁴; *tert*-butyl alcohol, 1.946 \times 10⁴, 0.259 \times 10⁴. Extinction coefficients at 366.0 nm in benzene are azulene, 23.7, and benzophenone, 67.

Fluorescence Spectra. Fluorescence spectra were recorded using a Perkin-Elmer-Hitachi MPF-2A spectrophotometer (Phototube, Hitachi R-106). Wavelength calibration of the emission monochromator was achieved using a mercury pen-ray lamp.⁵⁸ A calibrated General Electric 30A/T24/7 tungsten ribbon-filament lamp was used to obtain relative emission intensity correction factors.^{59,60} Relative fluorescence quantum yields of *trans*-stilbene were determined at 24° using 1-cm square cells. Solution concentrations (\sim 4 \times 10⁻⁵ *M*) were adjusted to the same optical density (1.00 \pm 0.02) at the excitation wavelength, 305.0 nm. Fresh solutions were used in duplicate measurements because loss of about 5% of the emission intensity, probably due to *trans* \rightarrow *cis* photoisomerization, occurred during the recording of each spectrum. Rela-

tive fluorescence quantum yields were determined by cutting and weighing Xerox copies of the corrected fluorescence spectra.

Irradiation Procedures. Samples (3 ml) of solutions containing the desired substrate in the presence or absence of sensitizer and/or quencher were introduced into 13 \times 60 mm Pyrex ampoules which were equipped with grease traps and 10/30 female joints. Prior to use, the ampoules were washed once with concentrated NH₄OH, repeatedly with distilled water, and oven-dried. The solutions were degassed in three-four freeze-pump-thaw cycles to about 10⁻⁶ Torr, and the ampoules were flame sealed at a constriction. The total stilbene concentration was 1.00 \times 10⁻² *M* for all photostationary state measurements. In most cases photostationary states were approached from both sides. In some cases, irradiation times were minimized by using *trans*- and *cis*-stilbene mixtures which bracketed the expected stationary states. Benzophenone-sensitized irradiations and initial isomerization rate experiments were carried out in a merry-go-round apparatus.⁶¹ Fluorenone-sensitized and most direct excitation irradiations were carried out by strapping the ampoules to the outer wall of a Hanovia probe, or to the outer wall of a Pyrex reactor well containing distilled water and the probe and lamp. The latter procedure allows placement of more samples about the lamp. In all cases the samples were immersed in a water bath thermostated at 30.2 \pm 0.1°. A 450-W Hanovia 679A "high-pressure" mercury lamp was employed.

Filter Systems. Four filter systems were employed for the above irradiations. (1) The first was a cylindrical uranium glass filter which transmits light of wavelengths longer than 3200 Å. (2) The second system was a combination of Corning CS 7-37 and 0-52 glass filters, transmitting only the group of mercury lines at 366.0 nm. (3) The third system consisted of a water solution containing 0.76 g of K₂Cr₂O₇ and 15.38 g of K₂CO₃ per 500 ml. A 1-cm path length (0.9–1.0-cm path lengths were employed) of this solution transmits 0.42 and 10.1% of the mercury lines at 302.5 and 313.0 nm, respectively, as well as light of wavelengths longer than 450.0 nm. (4) The fourth system was identical with the third except for the addition of Corning glass color filters C.S. 7-54. The glass filters do not affect transmission at 302.5 and 313.0 nm, but completely absorb all visible light. It should be noted that information supplied by Hanovia indicates that the relative output of a 450-W lamp at 313.0 and 302.5 nm is 13.2:7.2. Transmission spectra of filter systems 1–4 are recorded in ref 60.

Acknowledgment. This research was supported by National Science Foundation Grants GP-7941 and GP-24265.

(61) F. G. Moses, R. S. H. Liu, and B. M. Monroe, *Mol. Photochem.*, **1**, 245 (1969).

(57) We thank M. N. V. McElvar for the calibration.

(58) We thank Dr. R. H. Johnsen for the use of this lamp.

(59) We thank Dr. J. T. Vickers for the use of this lamp.

(60) For details see E. D. Megarity, Ph.D. Thesis, Florida State University, 1969, Tallahassee, Fla. 32306.

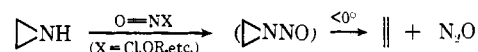
Origin of the Instability of *N*-Nitrosoaziridines

William L. Mock* and Peter A. H. Isaac

Contribution from the Department of Chemistry, Carnegie-Mellon University, Pittsburgh, Pennsylvania 15213. Received July 19, 1971

Abstract: *N*-Nitroso-9-azabicyclo[4.2.1]nona-2,4,7-triene (2), considered to be a 1,6 adduct of cyclooctatetraene and nitrous oxide, was prepared and found to be thermally stable toward fragmentation. In light of this result the facile cleavage of *N*-nitrosoaziridines to olefins and nitrous oxide is regarded as a consequence of ring strain and associated rehybridization effects which predispose the latter substances toward a particular mode of "nonlinear" chelotropic cycloreversion.

The nitrosation of ethylenimine derivatives and the ensuing facile fragmentation of the intermediate *N*-nitrosoaziridines to olefins and nitrous oxide represents a synthetic sequence of some utility.¹ Mech-



(1) (a) C. L. Bumgardner, K. S. McCallum, and J. P. Freeman, *J. Amer. Chem. Soc.*, **83**, 4417 (1961); (b) W. Rundel and E. Müller,

Chem. Ber., **96**, 2528 (1963); (c) R. D. Clark and G. K. Helmkamp, *J. Org. Chem.*, **29**, 1316 (1964). The uses of this reaction for alkene synthesis and *cis*-*trans* olefin isomerization have been indicated: (d) R. M. Carlson and S. Y. Lee, *Tetrahedron Lett.*, 4001 (1969).