tinous precipitate formed. The CH_2Cl_2 solution was decanted and the solid washed further with 3 × 10 mL of CH_2Cl_2. The combined extracts were dried over $MgSO_4$, evaporated in vacuo and distilled at 100 °C (30 mmHg) to give a pale brown oil **22**: yield 0.293 g (67%); ^1H NMR ($CDCl_3$, 60 MHz) δ 4.99 (br s, 2 H), 7.40 (d, 1 H, $J = 4$ Hz), 7.78 (d, 1 H, $J = 7$ Hz); ^{13}C NMR ($CDCl_3$) 43.28 (t), 120.60 (d), 143.30 (d), 160.98 (s), 161.12 (s); IR (neat) 3100, 3080, 2960, 2920, 2140, 1498, 1430, 1322, 1255, 1180, 1140, 1050, 940, 770, 730 cm^{-1}; UV (95%, EtOH), λ_{max} 240, 210 (ϵ 4300, 2700). Anal. Calcd for $C_5H_4N_2S$: C, 48.38; H, 3.22. Found: C, 47.94; H, 3.26.

13-Demethyldysidenin (3) and 13-Demethylisodysidenin (4). In a 5-mL round-bottom flask containing 80 mg (0.42 mmol) of the aldehyde **16** dissolved in 0.5 mL of MeOH was added a solution of 87 mg (0.42 mmol) of the acid **17**, 50 mg (0.42 mmol) of the isonitrile (**22**), and 0.132 mL (0.42 mmol) of 3.2 M CH_3NH_2/MeOH in 1.5 mL of methanol. This mixture was stirred at room temperature for 65 h and then diluted with 20 mL of CH_2Cl_2 and extracted with 1 N HCl (2 × 5 mL) followed by 5% $NaHCO_3$ (1 × 5 mL). The organic phase was dried over $MgSO_4$ and evaporated in vacuo to give a brown oil. The oil was flash chromatographed over silica eluting with 45% hexanes/55% ethyl ether to give 69 mg (0.13 mmol) of a mixture of **3** and **4**, yield 30.7%. This mixture was separated by HPLC using a Waters 5μ Silica Radial Pak Cartridge eluting with 65% diethyl ether/35% hexanes at 3 mL/min. The compound 13-demethyldysidenin (**3**) eluted at 4.83 min and 13-demethylisodysidenin (**4**) eluted at 5.55 min. A total of 29.5 mg of 13-demethylisodysidenin and 37.3 mg of 13-demethyldysidenin was recovered from this chromatography. Spectral data for these compounds are given as follows.

13-Demethyldysidenin (3): $[\alpha]^{14}{}_D$ +96.07° ($CHCl_3$, *c* 0.41); ^1H NMR ($CDCl_3$, 250 MHz) δ 1.36 (d, 3 H, $J = 6.34$ Hz), 1.36 (d, 3 H, $J = 6.39$ Hz), 1.93 (ddd, 1 H, $J = 4.1, 10.5, 14.6$ Hz), 2.24 (m, 1 H), 2.49 (dd, 1 H, $J = 9.2, 16.1$ Hz), 2.64 (dd, 1 H, $J = 13.1, 14.4$ Hz), 3.01 (s, 3 H), 3.11 (dd, 1 H, $J = 2.4, 16.3$ Hz), 3.31 (m, 1 H), doublet of ABq, A 4.62 (1 H, $J = 5.3, 16.1$ Hz), B 4.84 (1 H, $J = 6.5, 16.1$ Hz), 5.41 (dd, 1 H, $J = 4.16, 11.8$), 7.13 (brt, 1 H, $J = 5.51$ Hz), 7.28 (d, 1 H, $J = 3.23$ Hz), 7.69 (d, 1 H, $J = 3.27$ Hz); ^{13}C NMR ($CDCl_3$) 16.25, 17.20, 30.65, 30.65, 37.47, 40.73, 51.52, 51.88, 53.91, 105.18, 105.48, 119.26, 142.44, 166.50, 169.44, 172.10; IR ($CHCl_3$) 3400, 2985, 2920, 1675, 1632, 1510, 1455, 1378, 1298, 1267, 1250, 1140, 1100, 1062, 960, 905 cm^{-1}; UV (95% EtOH) λ_{max} 201 (ϵ 15 500); mass spectra (EI) *m/e* 533 (M), 496, 390, 382, 356, 202 (base peak), 166, 141, 123, 113, 98, 57, 42.

13-Demethylisodysidenin (4): $[\alpha]^{15}{}_D$ −48.5° ($CHCl_3$, *c* 0.59); ^1H NMR ($CDCl_3$, 250 MHz), δ 1.33 (d, 1 H, $J = 6.5$ Hz), 1.38 (d, 1 H, $J = 6.5$ Hz), 1.49 (ddd, 1 H, $J = 4.5, 9.9, 13.4$ Hz), 2.47, (dd, 1 H, $J = 9.3, 16.2$ Hz), 2.65 (m, 1 H), 2.94 (ddd, 1 H, $J = 2.6, 10.3, 13.0$ Hz), 3.02 (s, 3 H), 3.06 (dd, 1 H, $J = 2.5, 17.5$ Hz), 3.27 (m, 1 H), doublet of ABq, A 4.65 (1 H, $J = 16.1, 5.3$ Hz), B 4.87 (1 H, $J = 16.1, 6.7$ Hz), 5.31 (dd, 1 H, $J = 4.7, 10.2$ Hz), 7.13 (brt, 1 H, $J = 5.6$ Hz), 7.29 (d, 1 H, $J = 3.3$ Hz), 7.69 (d, 1 H, $J = 3.3$ Hz); ^{13}C NMR ($CDCl_3$) 16.6, 17.42, 31.37, 37.58, 40.78, 51.76, 51.86, 54.72, 105.24, 105.53, 119.39, 142.49, 166.80, 169.27, 171.65; IR ($CHCl_3$) 3400, 2990, 2935, 1680, 1510, 1456, 1413, 1400, 1380, 1290, 1240, 1140, 1120, 1065, 955, 905, 870, 840 cm^{-1}; UV (95% EtOH) λ_{max} 202 (ϵ 14 000); mass spectrum (EI) *m/e* 496, 390, 382, 202 (base peak), 166, 149, 141, 98, 57, 42.

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One-Way Photoisomerization of *cis*-Stilbene via a Cation Radical Chain Mechanism

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Abstract: Quenching of singlet 9,10-dicyanoanthracene by *cis*- or *trans*-stilbene in acetonitrile solution leads to a steady-state mixture consisting of 98.8% *trans*- and 1.2% *cis*-stilbene. Quantum yields for isomerization of *cis*-stilbene increase with increasing stilbene concentration, solvent polarity, salt concentration, and decreasing light intensity. These effects are attributed to a cation radical chain process in which the *cis*-stilbene cation radical isomerizes to the more stable *trans*-stilbene cation radical, which undergoes electron hole transfer to neutral *cis*-stilbene in competition with back electron transfer to the dicyanoanthracene anion radical. One-electron oxidation of *cis*-stilbene substantially lowers the activation energy for isomerization. In the presence of oxygen, the cation radical isomerization mechanism is suppressed and photooxygenation of *cis*- and *trans*-stilbene occurs.

The cation radicals of unsaturated and strained hydrocarbons undergo a variety of isomerization and cycloaddition reactions with activation energies substantially lower than those of the neutral molecules.[1-3] Generation of cation radicals via electron transfer to an electronically excited electron acceptor can result in quantum yields for cation radical isomerization or cyclodimerization in excess of unity.[3a] For example, Evans[4] observed that the naphthalene-sensitized isomerization of hexamethyl(Dewar benzene) to hexamethylbenzene in polar solvent can occur with high quantum yield ($\Phi \sim 80$ for 1.7 M reactant) as a consequence of a cation radical chain process (Scheme I). Electron-transfer from the Dewar benzene (D) to naphthalene

Scheme I. Cation Radical Chain Mechanism for the Naphthalene (A)-Sensitized Isomerization of Hexamethyl(Dewar benzene) (D) to Hexamethylbenzene (B)

$$A^* + D \rightarrow A^{-\cdot} + D^{+\cdot}$$

$$D^{+\cdot} \rightarrow B^{+\cdot}$$

$$D + B^{+\cdot} \rightarrow D^{+\cdot} + B$$

Scheme II. Electron-Transfer-Initiated Isomerization of a Trans Olefin via Formation of the Olefin Triplet

$$^*A^1 + t\text{-D} \rightarrow {}^1(A^{-}\cdot t\text{-D}^{+}\cdot)^* \rightarrow {}^3(A^{-}\cdot t\text{-D}^{+}\cdot)^* \rightarrow A + {}^3t\text{-D} \rightarrow c\text{-D}$$

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Table I. Fluorescence Quenching and Isomerization Quantum Yield Data

isomer	solvent	$k_q\tau^a$	$10^{-10}k_q$,^{b} M^{-1} s^{-1}	Φ_i^c
t-S	C_6H_6	115	0.93	0.011
t-S	CH_3CN	316	2.1	0.002
c-S	C_6H_6	75	0.60	0.11 (0.22)^d
c-S	THF			0.07
c-S	CH_3CN	387	2.5	0.32 (>10)^d
c-S	$(CH_3)_2SO$			0.41

^{a}Slope of a linear Stern–Volmer plot for quenching of the fluorescence of 2×10^{-5} M DCA in deoxygenated solution. ^{b}Calculated from $k_q\tau$ and literature values[13] for τ in benzene (12.4 ns) and acetonitrile (15.2 ns) solution. ^{c}Quantum yields for isomerization of deoxygenated solutions of 10^{-3} M DCA and 0.05 M stilbene. ^{d}Extrapolated to infinite *c*-S concentration from the intercepts in Figure 2.

(A) generates a Dewar benzene cation radical ($D^{+}\cdot$), which isomerizes to yield the benzene cation radical ($B^{+}\cdot$). Nearly isoenergetic electron transfer from D to $B^{+}\cdot$ results in chain propagation, while reaction of $B^{+}\cdot$ or $D^{+}\cdot$ with impurities leads to termination of the chain process.

Electron-transfer-initiated isomerization of olefins can occur via either of two mechanisms.[3a,5] When the triplet energy of the olefin is lower than that of the exciplex or contact radical ion pair ($A^{-}\cdot D^{+}\cdot$), the olefin triplet can be populated via intersystem crossing of a singlet radical ion pair or homogeneous reencounter of the free radical ions.[6] The olefin triplet will decay to yield the same mixture of isomers with the same limiting quantum yields as obtained in triplet-sensitized olefin isomerization (Scheme II). This mechanism has been reported for the isomerization of 1,2-diarylolefins, including *trans*-stilbene, which possess low-energy triplet states.[5,7] Alternatively, olefin isomerization can occur via a cation radical chain mechanism analogous to Scheme I, as initially proposed by Roth and Shilling[5] to account for the stronger CIDNP effect observed upon triplet chloranil quenching by *cis*- vs. *trans*-1-phenylpropene. A modified version of Scheme I was proposed to account for singlet triphenylene-*p*-dicyanobenzene cosensitized isomerization of *trans*- and *cis*-1-phenoxypropene, which is reported to occur in both directions with limiting quantum yields near unity to yield a 1:1 photostationary state isomer mixture.[8] The 9,10-dicyanoanthracene-sensitized isomerization of 1,2-diarylcyclopropanes is also proposed to occur via a cation radical chain process.[9]

In the course of our investigation of the formation and decay of the *trans*-stilbene (*t*-S) radical ions,[10] we have observed that electron-transfer quenching of singlet 9,10-dicyanoanthracene (DCA) by *t*-S results in inefficient isomerization, whereas quenching by *cis*-stilbene (*c*-S) results in nearly quantitative isomerization to *t*-S. Investigation of the mechanism of this unusual one-way photoisomerization process indicates that it occurs via a cation radical chain mechanism in which the activation energy for cation radical isomerization is substantially lower than that for neutral *c*-S. In the presence of molecular oxygen, the cation radical chain isomerization process is inhibited and the photooxygenation process previously reported by Foote and coworkers[11] observed.

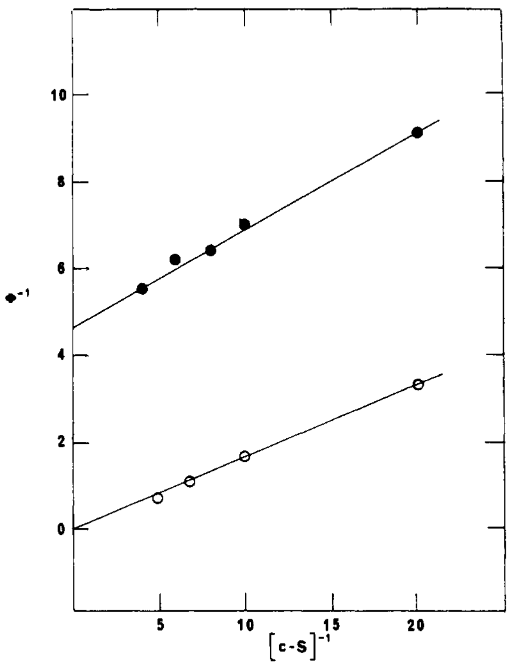

Figure 1. Double-reciprocal plot for the concentration dependence of the *cis*-stilbene isomerization quantum yield in acetonitrile (○) and benzene (●) solution.

Table II. Effects of Light Intensity and Added Salt on the Quantum Yield for *cis*-Stilbene Isomerization

solvent	$10^8 I^0$, einstein s^{-1}	$NaClO_4$, M	$\Phi_{c,t}{}^a$
C_6H_6	1.2		0.17
C_6H_6	7.4		0.11
CH_3CN	1.2		2.7^b
CH_3CN	7.4		1.5^b
CH_3CN	7.4		0.32
CH_3CN	7.4	0.17	0.50
CH_3CN	7.4	0.49	0.51

^{a}Quantum yields for *trans*-stilbene formation. Reaction conditions as in Table I, note *c*, expected as noted. ^{b}Data for 0.3 M *cis*-stilbene.

Results

Stilbene Isomerization. The fluorescence of DCA is reported to be quenched by *t*-S[12] and 1,1-diphenylethylene[13] with rate constants comparable to the rate of diffusion[14] in benzene ($k_{diff} = 1.6 \times 10^{10}$ M^{-1} s^{-1}) and acetonitrile ($k_{diff} = 2.9 \times 10^{10}$ M^{-1} s^{-1}) solution. Similar results are obtained upon quenching of DCA by *c*-S (Table I). Weak exciplex emission is observed at 560 ± 20 nm upon quenching of DCA by *t*-S but not by *c*-S in benzene solution.

Irradiation of DCA (10^{-3} M) and *c*-S (0.05 M) in degassed acetonitrile solution with 365-nm light at 25 °C for several hours results in conversion to a mixture of 98.8 ± 0.2% *t*-S and 1.2 ± 0.2% *c*-S, the composition of which does not change upon further irradiation. Irradiation of DCA and *t*-S under comparable conditions results in <2% isomerization to *c*-S and little consumption of DCA or stilbenes. Irradiation of DCA and *c*-S in benzene solution results in slower isomerization to *t*-S than observed for acetonitrile solution, conversion to 76% *t*-S requiring 50-h irradiation. Since consumption of DCA and the stilbenes and yellowing of the solution was observed after such prolonged irra-

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Table III. Quantum Yields for Isomerization and Benzaldehyde Formation in the Absence and Presence of Oxygen

isomer, M	solvent	O_2, atm	$\Phi_i{}^a$	$\Phi_{BA}{}^b$
t-S (0.05)	C_6H_6	0	0.011	0
t-S	C_6H_6	1.0	0.032	0
t-S	CH_3CN	0	0.002	0
t-S	CH_3CN	1.0	0.011	0.18
c-S	C_6H_6	0	0.11	0
c-S	C_6H_6	1.0	0.21	0
c-S	CH_3CN	0	0.32	0
c-S	CH_3CN	0.25	*c*	0.076
c-S	CH_3CN	1.0	0.065	0.12
c-S (0.10)	CH_3CN	1.0	0.071	0.11
c-S (0.15)	CH_3CN	1.0	0.080	0.11

[a] Quantum yields determined as in Table I, note *c*. [b] Quantum yield for benzaldehyde formation in air or oxygen saturated solution. [c] Not determined.

Table IV. Effects of Light Intensity and Added Salt on the Quantum Yield for Benzaldehyde Formation in Acetonitrile Solution

isomer	$10^8 I^0$, einstein s^{-1}	$NaClO_4$, M	$\Phi_{BA}{}^a$
t-S	1.2		0.14
t-S	7.4		0.18
c-S	1.2		0.063
c-S	7.4		0.12
c-S	7.4	0.17	0.032

[a] See Table III, note *b*.

diation, the true photostationary state in benzene solution could not be determined. Under the reaction conditions all of the incident light is absorbed by DCA and no isomerization is observed in its absence.

Quantum yields for the DCA-sensitized isomerization of *t*-S and *c*-S in several solvents measured at low (<10%) conversion of the initial isomer using monochromatic 365-nm irradiation are reported in Table I. Quantum yields for *t*-S → *c*-S isomerization are independent of *t*-S concentration; however, values for *c*-S → *t*-S isomerization increase with increasing *c*-S concentration in both benzene and acetonitrile solution, as shown in Figure 1. The intercepts of Figure 1 provide values for the isomerization quantum yield in the limit of infinite *c*-S concentration of 0.22 and >10 in benzene and acetonitrile solution, respectively.

The quantum yields for DCA-sensitized isomerization of *c*-S in both benzene and acetonitrile solution increase with decreasing light intensity. Addition of $NaClO_4$ to acetonitrile solutions of DCA and *c*-S results in an increase in the isomerization quantum yield. Quantum yield data for light intensity and salt effects is summarized in Table II. The quantum yield for DCA-sensitized isomerization of *c*-S is also temperature dependent, decreasing by a factor of 10 between 48 and 0 °C.

Stilbene Photooxygenation. Irradiation of DCA and either *t*-S or *c*-S in benzene solution results in enhanced isomerization quantum yields (Table III) but no formation of photooxygenation products. Irradiation in acetonitrile solution at low conversions (<20%) results in stilbene isomerization and the formation of benzaldehyde, stilbene oxides, and benzil, as previously reported by Eriksen and Foote.[11b] Phenanthrene is also detected as a trace product (<1%) in the presence or absence of oxygen. Quantum yields for isomerization and benzaldehyde formation for solutions purged with nitrogen, air, and oxygen are reported in Table III. The quantum yield for disappearance of *c*-S for the last three entries in Table III is 0.20 ± 0.02, in excellent agreement with the value reported by Eriksen and Foote.[11b] Quantum yields for benzaldehyde formation from both *t*-S and *c*-S increase with increasing light intensity. Added $NaClO_4$ decreases the quantum yield for benzaldehyde formation from *c*-S. Quantum yield data for the light intensity and salt effects on benzaldehyde formation is summarized in Table IV.

Discussion

The cis,trans photoisomerization of stilbene has been the subject of extraordinary scrutiny.[15] Photostationary states enriched in the thermodynamically less stable ($\Delta H° = 2.3$ kcal/mol[16]) cis isomer are normally obtained upon direct irradiation, triplet sensitization, and irradiation of charge-transfer complexes.[15,17] In contrast, irradiation of DCA in the presence of *t*-S or *c*-S in acetonitrile solution results in the formation of a photostationary state mixture consisting of 98.8% *t*-S and 1.2% *c*-S, similar to the product mixture expected for thermal equilibration of the two isomers. Previous examples of the formation of trans-rich photostationary states upon "sensitized" irradiation of the stilbenes are limited to pyrylium salt dyes,[18a] triplet 9,10-dichloro-[18b] and 9-phenylanthracene[18c] in alcohol solvents, and palladium and platinum porphyrins.[18d] Triplet quantum chain mechanisms have been proposed for the latter reaction,[18d,e] as well as for the recently reported one-way photoisomerization of sterically congested aryl olefins.[19] Irradiation of the stilbenes in the presence of free radical initiators such as iodine or diphenyl disulfide is also known to effect cis → trans isomerization.[20] While triplet quantum chain and free radical mechanism must be considered (vide infra), we favor a cation radical chain mechanism of the DCA-sensitized isomerization of the stilbenes.

Scheme III. Cation Radical Chain Mechanism for Cis → Trans Isomerization of Stilbene

$$^1DCA^* + c\text{-}S \rightarrow DCA^{-}\cdot + c\text{-}S^{+}\cdot \tag{1}$$

$$c\text{-}S^{+}\cdot \rightarrow t\text{-}S^{+}\cdot \tag{2}$$

$$t\text{-}S^{+}\cdot + c\text{-}S \rightarrow t\text{-}S + c\text{-}S^{+}\cdot \tag{3}$$

$$DCA^{-}\cdot + t,c\text{-}S^{+}\cdot \rightarrow DCA + t,c\text{-}S \tag{4}$$

The observation of DCA-sensitized one-way photoisomerization of *c*-S to *t*-S is consistent with an electron-transfer cation radical chain mechanism (Scheme III) analogous to that for valence isomerization of hexamethyl(Dewar benzene) (Scheme I). The observation of diffusion-controlled quenching of DCA fluorescence by *t*-S or *c*-S (Table I) and the detection of $DCA^{-}\cdot$ and $TS^{+}\cdot$ radical ions by transient absorption[21] and resonance Raman spectroscopy[10f] in acetonitrile solution support the occurrence of electron transfer from singlet DCA to *t*-S or *c*-S as the initial step in the isomerization mechanism (eq 1). The free energy of electron transfer to singlet DCA ($E_s = 2.88$ eV, $E_{1/2}{}^{red} = -0.89$ V)[3a] from *t*-S ($E_{1/2}{}^{ox} = 1.50$ V) or *c*-S ($E_{1/2}{}^{ox} = 1.59$ V)[22] in acetonitrile solution can be estimated using Weller's equation (eq 5).[23] The

$$\Delta G = -E_s - E_{1/2}{}^{red} - E_D{}^{ox} - 0.06 \text{ eV} \tag{5}$$

values calculated for *t*-S and *c*-S (−0.55 and −0.46 eV, respectively) are substantially exothermic, in accord with the proposed electron-transfer mechanism.

The second step in the proposed reaction mechanism is isomerization of $c\text{-}S^{+}\cdot$ to $t\text{-}S^{+}\cdot$. While $c\text{-}S^{+}\cdot$ has been observed by absorption spectroscopy in frozen matrices at 77 K, it isomerizes to $t\text{-}S^{+}\cdot$ upon irradiation or warming of the matrix.[24a,b] Only $t\text{-}S^{+}\cdot$

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is observed following low-energy electron impact of *t*-S or *c*-S in the vapor phase.[24c] In the absence of information about the lifetime of *c*-$S^{+}\cdot$ in solution, we assume that its isomerization, like that of *c*-$S^{-}\cdot$, is rapid and essentially irreversible.[25] One-way isomerization of *c*-$S^{+}\cdot$ to *t*-$S^{+}\cdot$ has also been reported to occur upon chemical oxidation of *c*-S with Mn(III)OAc_3[1] and upon photosensitized isomerization of *N*-methyl-4-(β-styryl)pyridinium iodides.[26]

The third step in the proposed reaction mechanism is electron hole transfer from *c*-S to *t*-$S^{+}\cdot$ (eq 3). On the basis of the oxidation potentials of *c*-S and *t*-S, this step should have an activation energy of ≥0.09 eV and occur with a rate constant slower than that for diffusion.[27a] While electron hole transfer should occur reversibly, rapid unimolecular isomerization of *c*-$S^{+}\cdot$ (k_2) may render the reverse reaction kinetically insignificant. The second and third steps of Scheme III constitute a cation radical chain mechanism for the isomerization of neutral *c*-S to *t*-S. While isomerization of *c*-S has been proposed to occur via an anion radical chain process,[27b] the cation radical chain process has not previously been reported.[26b]

The final step of the proposed reaction mechanism is back electron transfer from $DCA^{-}\cdot$ to *t*-$S^{+}\cdot$ or *c*-$S^{+}\cdot$ (eq 4), which terminates the cation radical chain process. Decay of *t*-$S^{+}\cdot$ transient absorption[12] and Raman[10f] signals is reported to follow second-order kinetics under the high intensity conditions of pulsed laser excitation. First-order decay of *t*-$S^{+}\cdot$ or *c*-$S^{+}\cdot$ by reactions with neutral reactants or impurities might be expected to compete with second-order processes at the low light intensity conditions used for quantum yield determinations.

The cation radical chain mechanism of Scheme III readily accounts for the effect of *c*-S concentration, temperature, light intensity, solvent polarity, added $NaClO_4$, and O_2 upon the isomerization efficiency. Increasing the *c*-S concentration should permit the chain-propagating electron hole transfer process (eq 3) to compete more effectively with chain-terminating back electron transfer (eq 4). As seen in Figure 1, the intercept of a plot of Φ^{-1} vs. $[c\text{-S}]^{-1}$ in acetonitrile solution has an extrapolated intercept near zero, indicative of a long chain process in the limit of high *c*-S concentration. Increasing the temperature should also increase the rate of the endothermic electron hole transfer process (eq 3). Decreasing the light intensity permits the chain propagation process, which is first order in radical ion concentration, to compete more effectively with chain termination, which is second order in radical ion concentration and hence light intensity dependent. The observed increase in the isomerization quantum yield with decreasing light intensity suggests that at least part of the chain termination occurs by a second-order process.[28] The quantum yield data in Figure 1 indicates that the rate constants for chain-termination processes must be substantially larger than the rate constant for endothermic electron hole transfer in view of the significantly higher concentrations of *c*-S vs. $DCA^{-}\cdot$ present under the reaction conditions.

The increase in *c*-S isomerization quantum yields with increasing solvent polarity (Table I) is indicative of the involvement of free *c*-$S^{+}\cdot$ in the isomerization process. Yields of ionic photodissociation of pure charge-transfer exciplexes are known to increase with increasing solvent polarity.[29] Both the lifetime of *c*-$S^{+}\cdot$ and the rate of its isomerization to *t*-$S^{+}\cdot$ (eq 2) should be greater for the free cation radical formed upon ionic photodissociation in polar solvent than for the exciplex (contact radical ion pair) formed in nonpolar solvent. Ion pair formation between the anion radical of *c*-S and alkali cations is known to substantially retard its rate of isomerization to *t*-$S^{-}\cdot$.[30] Even in the nonpolar solvent benzene, isomerization of *c*-S is concentration dependent (Figure 1) and substantially more efficient than isomerization of *t*-S. This suggests that a cation radical chain mechanism may occur in nonpolar solvent, possibly due to interception of the exciplex by a second molecule of *c*-S or via a small, but finite, yield of ionic photodissociation in nonpolar solvent.[29]

Salt effects provide an additional probe of the role of radical ion intermediates in the isomerization process. Evans[4] observed an increase in the quantum yield for the cation radical chain isomerization of hexamethyl(Dewar benzene) in the presence of sodium or lithium perchlorate but did not comment on the origin of the salt effect. McCullough and Yeroushalmi[31] have reported that added $LiClO_4$ reduces the exciplex lifetime and cycloaddition efficiency of the 1-naphthonitrile–tetramethylethylene exciplex in moderately polar solvents. They attributed the salt effect to an increased rate of exciplex ionic photodissociation. Simon and Peters[32] have investigated the dynamics of ion pair exchange between the benzophenone–diethylaniline ($BP^{-}\cdot DMA^{+}\cdot$) solvent-separated radical ion pair and $NaClO_4$ in acetonitrile solution and report a rate constant of $7 \times 10^8\ M^{-1}\ s^{-1}$ for formation of $Na^{+}BP^{-}\cdot$. In addition to increasing the yield of exciplex ionic dissociation, added salts can prolong the lifetime of the free radical ions. For example, the reactivities of aromatic anion radicals with solvated electrons in tetrahydrofuran solution are reduced upon ion pair formation with alkali-metal cations.[33] In view of the rapid rate of exciplex ionic photodissociation in acetonitrile solution[29] and the observation of similar salt effects for 0.17 and 0.49 M $NaClO_4$, it seems likely that the observed salt effect reflects a reduced rate of back electron transfer from $Na^{+}DCA^{-}\cdot$ vs. free $DCA^{-}\cdot$ to *t*-$S^{+}\cdot$ or *c*-$S^{+}\cdot$, rather than an enhanced yield of ionic photodissociation.

The cation radical chain isomerization mechanism of Scheme III should result in the establishment of equilibrium between neutral *t*-S and *c*-S. In fact the photostationary state obtained in acetonitrile solution (98.8% *t*-S) does not differ appreciably from the calculated value for thermal room temperature equilibrium (99.8% *t*-S).[16] The photostationary state can be calculated from the kinetic data and low-conversion quantum yields from Table I using eq 6,[15] where the subscripts refer to the reactant

$$\frac{[c\text{-S}]}{[t\text{-S}]} = \frac{k_{qt}}{k_{qc}} \frac{\Phi_t}{\Phi_c} \qquad (6)$$

isomer. The calculated photostationary state in acetonitrile solution is 99.5% *t*-S, closer to the thermal equilibrium value than is the observed value.

Alternative mechanisms for the one-way photoisomerization of *c*-S include the previously described triplet quantum chain[18,19] and the free radical[20] mechanisms. The triplet chain mechanism of Mercer-Smith and Whitten[18d] would presumably require intersystem crossing of the DCA–*c*-S singlet exciplex, or radical ion pair, to yield a triplet exciplex which can undergo isomerization and dissociation to yield *t*-S and $^3DCA^*$, which could, in turn, sensitize the isomerization of *c*-S or *t*-S. This mechanism would be expected to yield only slightly reduced values of $\Phi_{t,c}$ and values of $\Phi_{c,t}$ independent of *c*-S concentration (at sufficiently high concentrations for efficient triplet quenching),[18d] predictions at variance with the observed results. While the observed solvent effect on $\Phi_{c,t}$ might be rationalized as resulting from variable yields of exciplex or radical ion pair intersystem crossing, the observed

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[25] Spada and Foote[21] attributed transient absorption at 515 nm to *c*-$S^{+}\cdot$ formed upon DCA sensitized oxidation of *c*-S. In view of the spectroscopic studies of ref 24 and our mechanistic investigations it seems highly unlikely that *c*-$S^{+}\cdot$ has a long enough lifetime to be detcted on the microsecond time scale at room temperature in solution.

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[28] In contrast, Evans[4] observed that the quantum yield for Dewar benzene isomerization is independent of light intensity.

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Scheme IV. Foote's Mechanism for Stilbene Photooxygenation

$$^1\mathrm{DCA}^* + t\text{-S} \rightarrow {}^1\mathrm{DCA}^{-\cdot} + t\text{-S}^{+\cdot}$$

$$\mathrm{DCA}^{-\cdot} + \mathrm{O}_2 \rightarrow \mathrm{DCA} + \mathrm{O}_2^-$$

$$t\text{-S}^{+\cdot} + \mathrm{O}_2^- \rightarrow \text{oxidation products}$$

effects of light intensity and added salt are difficult to reconcile with such a triplet chain mechanism. The triplet chain mechanism of Tokumaru[19] requires adiabatic triplet cis,trans isomerization followed by energy transfer from the planar triplet trans isomer to the cis isomer, processes that are not observed for stilbene triplets,[18e] and fails to rationalize the effects of light intensity and salt in the present reactions. Finally, a free radical mechanism can be excluded on the basis of its failure to rationalize the effects of solvent polarity and added salt as well as the absence of an obvious candidate for the free radical intermediate.

irradiation of DCA with *t*-S or *c*-S in oxygenated benzene solution results in larger isomerization quantum yields than those obtained in the absence of oxygen (Table III), but no detectable photooxygenation products. Oxygen enhancement of *t*-S isomerization via the exciplexes of *t*-S with amines and fumaronitrile has been previously observed and attributed to oxygen-catalyzed exciplex intersystem crossing to yield triplet *t*-S.[7,10f] Intersystem crossing of the DCA–*t*-S exciplex should yield more of the lower energy DCA triplet (1.8 eV) vs. *t*-S triplet (2.12 eV) thus accounting for the low yield of *t*-S isomerization in the absence or presence of oxygen.[10f] Oxygen might also react with the singlet exciplex so as to suppress back electron transfer without causing photooxygenation, as observed for the DCA-sensitized isomerization of 1,2-diarylcyclopropanes.[9]

Irradiation of DCA with *t*-S or *c*-S in oxygenated acetonitrile solution results in the formation of isomerized stilbene and the photoxidation products benzylaldehyde, stilbene oxides, and benzil, previously observed by Foote.[11] The mechanism of photooxygenation proposed by Foote[11b] is outlined in Scheme IV. The initial step is the same as in Scheme III and is followed by electron transfer from $\mathrm{DCA}^{-\cdot}$ to oxygen to form the superoxide radical anion. The final step is the reaction of t-$\mathrm{S}^{+\cdot}$ with O_2^- to form oxidation products. While t-$\mathrm{S}^{+\cdot}$ can also react with O_2 to form oxidation products,[34] the observation that the quantum yield for benzaldehyde formation from *c*-S increases with increasing light intensity (Table IV) indicates that at least part of the benzaldehyde is formed via a process that is second order in light-generated intermediates, in accord with the superoxide mechanism. Furthermore, the quantum yield for benzaldehyde formation from *c*-S is only 50% larger for oxygen- vs. air-saturated solutions. A larger increase might have been expected for the reaction of stilbene cation radicals with O_2.[34] The addition of NaClO_4 to oxygenated acetonitrile solutions of DCA and *c*-S results in a substantial decrease in the quantum yield for benzaldehyde formation (Table IV). If the salt served only to increase the yield of ionic photodissociation, then an increase in quantum yield similar to that observed for *c*-S isomerization (Table II) might have been expected. Formation of a $\mathrm{Na}^+\mathrm{DCA}^{-\cdot}$ ion pair should slow down the rate of O_2^- formation and thus inhibit photooxygenation, if O_2^- rather than O_2 reacts with c-$\mathrm{S}^{+\cdot}$

The quantum yield for isomerization of *c*-S is substantially lower in the presence vs. absence of O_2 in acetonitrile solution, whereas the value for *t*-S is higher (Table III). The second-order decay of t-$\mathrm{S}^{+\cdot}$ as determined by transient absorption[12] and Raman spectroscopy[10f] is faster in the presence vs. absence of O_2, indicating that reaction of t-$\mathrm{S}^{+\cdot}$ with O_2^- may be more rapid than back electron transfer to $\mathrm{DCA}^{-\cdot}$. Reaction of t-$\mathrm{S}^{+\cdot}$ or c-$\mathrm{S}^{+\cdot}$ with O_2^- will effect the termination of the cation radical chain process and lower the *c*-S isomerization quantum yield. The concentration dependence of the *c*-S isomerization quantum yield is much smaller in the presence (Table III) vs. absence (Figure 2) of oxygen, as expected if reaction of t-$\mathrm{S}^{+\cdot}$ or c-$\mathrm{S}^{+\cdot}$ with O_2^- is more rapid than cation radical chain propagation. The increase in the quantum yield for *t*-S isomerization in the presence of oxygen plausibly results from inhibition of the cation radical chain mechanism which could consume much of the *c*-S formed in the reaction of singlet DCA with *t*-S.

In summary, we propose that one-way isomerization of *cis*-stilbene to *trans*-stilbene occurs via a cation radical chain mechanism (Scheme III). This proposal is consistent with previous observations of relative CIDNP intensities and of isomerization of cis but not trans stereoisomers as a competing process in the oxygenation[5] and cycloaddition of aryl olefin cation radicals.[2b] It may also account for the previously unexplained results of stilbene isomerization using pyrylium salt dye sensitizers.[18a] The occurrence of isomerization at room temperature indicates that the activation energy for isomerization of c-$\mathrm{S}^{+\cdot}$ is substantially lower than that of neutral *c*-S (46 ± 2 kcal/mol[35]). The absence of significant phenanthrene formation in the absence or presence of oxygen indicates that cyclization of c-$\mathrm{S}^{+\cdot}$ to the dihydrophenanthrene cation radical either does not compete with isomerization to t-$\mathrm{S}^{+\cdot}$ or occurs reversibly. In the presence of oxygen the cation radical process is suppressed and photoxygenation (Scheme IV) occurs. The observation of similar quantum yields for benzaldehyde formation from *c*-S and *t*-S suggests that the efficiency of ionic photodissociation is similar for the two isomers. We are presently investigating the kinetics of the chain process of Scheme I and the effects of aryl olefin structure upon efficiencies and equilibria for cation and anion radical isomerization processes.

Experimental Section.

Materials. *trans*-Stilbene (Aldrich) was recrystallized once from benzene and twice from absolute ethanol. *cis*-Stilbene (Aldrich) was chromatographed on neutral alumina, distilled under vacuum, and contained 0.2% trans impurity by GC analysis. 9,10-Dicyanoanthracene (Eastman) was recrystallized from ethanol. Benzene (Aldrich, spectroquality) and acetonitrile (Burdick and Jackson) were refluxed over sodium and distilled.

Methods. Fluorescence quenching data were obtained for nitrogen-purged solutions of 2×10^{-5} M DCA and *cis*- or *trans*-stilbene ($\geq 10^{-2}$ M) by using a Perkin-Elmer MPF-44A spectrofluorimeter. Quantum yields for stilbene isomerization and benzaldehyde formation were determined for nitrogen- or oxygen-purged solutions of 10^{-3} DCA and *cis*- and *trans*-stilbene irradiated on a merry-go-round apparatus at 25 °C with monochromatic 365-nm light provided by the filtered (Corning 0-52 and 7-54 filters) output of a Hanovia medium-pressure mercury lamp in a water-cooled Pyrex lamp well. High and low light intensities were provided by a 450-W and 200-W lamp, respectively. Light intensities were determined by Amberchrome 540 actinometry.[36] Solutions were analyzed for product formation at low (<10%) conversions of *t*-S or *c*-S to products by using a calibrated column of 5% SF-96 on Chromosorb G with a Varian 3700 flame ionization gas chromatograph.

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