Cycloaddition Reactions of Stilbene–Electron-Poor-Alkene Exciplexes

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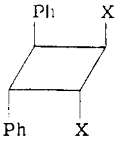
Abstract: The fluorescence of *trans*-stilbene is quenched by several electron-poor alkenes. Quenching by dimethyl fumarate and fumaronitrile is accompanied by the appearance of exciplex fluorescence in nonpolar solvents. Quenching constants increase with increasing alkene electron affinity, indicating that singlet stilbene acts as an electron donor in exciplex formation. The stilbene–dimethyl fumarate exciplex forms a single cycloadduct, dimethyl μ-truxinate, at low conversions. Evidence is also presented for inefficient addition of *cis*-stilbene and dimethyl fumarate to form selectively dimethyl neotruxinate. Excitation of the weak ground-state complexes of *trans*-stilbene with dimethyl fumarate and fumaronitrile results in the same chemical reactions and fluorescence which are observed upon diffusive encounter of singlet *trans*-stilbene and ground-state alkene. Quenching of stilbene excimer by dimethyl fumarate results in the formation of an oxetane cycloadduct and not the cyclobutane formed from singlet stilbene (monomer) with dimethyl fumarate.

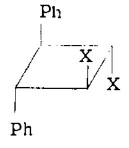
Electronic excitation enhances both the electron donor and acceptor properties of organic molecules.[2] As a result, excited-state complexes (exciplexes) have been observed for donor–acceptor pairs which do not form stable ground-state complexes. We have previously reported investigations of the photochemical and photophysical behavior of the exciplexes formed between electronically excited stilbenes and ground state dienes,[3] vinyl ethers,[4] and amines.[5] In these complexes the excited stilbene is the electron acceptor (A*) and the alkene or amine is the electron donor (D). We report here an investigation of the interactions between excited stilbenes and several electron-poor alkenes, in which stilbene serves as the electron donor (D*) and the alkene as the electron acceptor (A). Among the significant findings of this investigation are (a) stereoselective addition of both *trans*- and *cis*-stilbene singlets to dimethyl fumarate, (b) identical chemical and physical behavior of the *trans*-stilbene–dimethyl fumarate exciplex and excited ground-state complex, and (c) different cycloaddition products for quenching of *trans*-stilbene monomer and excimer by dimethyl fumarate.

Results and Discussion

***trans*-Stilbene (TS)–Dimethyl Fumarate (F).** Irradiation of TS (0.028 M) and F (0.28 M) in benzene solution yields exclusively dimethyl μ-truxinate (**1**) and isomerized stilbene (CS) at low conversions. After nearly complete conversion of TS to products, **1** ($X = CO_2CH_3$) was isolated in 46% yield along with lesser amounts of the isomeric δ- and *neo*-truxinates, **2** (trace) and **4** (6%).[6] Stilbene isomerization is more efficient than cycloaddition and the photostationary state (93% cis)[7] is established prior to extensive conversion to cycloadducts. Some isomerization of F to dimethyl maleate also occurs; however, F remains in large excess (>95%) to the end of the reaction.



1, μ



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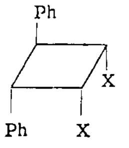
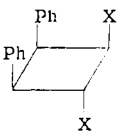
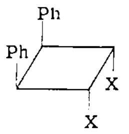


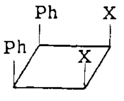
3, ζ



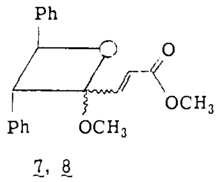
4, neo



5, β

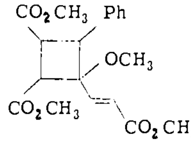


6, ω



7, 8

Preparative photolysis of a more concentrated solution of TS (0.20 M) and F (0.22 M) led to the formation of CS, truxinates **1** and **2**, and two additional adducts, characterized as isomeric oxetanes **7** and **8**. A small quantity of pyridine was added to the solutions to stabilize the oxetanes **7** and **8**. Control experiments showed the truxinate and oxetane products to be stable under the conditions used for subsequent quantitative studies ($\lambda_{ex} \geq 313$ nm, conversions <20% of TS) and GC analysis. Michler's ketone and benzil sensitize the isomerization of TS in the presence of F; however, no cycloadducts are observed even after the stilbene photostationary state is attained. In the pyridine-free preparative irradiations, a crystalline product was routinely obtained whose structure is assigned as **9**.[6] This unexpected and interesting byproduct formally represents a 2:1 adduct of F and TS which has lost benzaldehyde. We picture **9** as arising via oxetanes **7** and **8** through loss of benzaldehyde (detected by GC analysis) to give methoxydiene **10** (not isolated) which undergoes [2 + 2] photoaddition with a second molecule of F. Although the intermediacy of **10** remains to be proven and the stereochemistry of **9** has not been established, the relatively high yield of **9** and the absence of related or isomeric materials suggests a high degree of regio- and stereoselectivity in this reaction.



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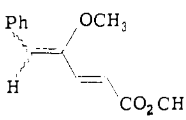

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The failure of triplet sensitization to effect either cyclobutane or oxetane formation establishes that singlet TS is a precursor of both cycloadducts. The complete retention of TS and F stereochemistry and the selective formation of **1** rather than the thermodynamically more stable truxinate **2** are

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Table I. Solvent Effects on the Reaction of *trans*-Stilbene (0.01 M) and Dimethyl Fumarate (0.20 M)

solvent (ϵ),[a,b] % THF in benzene	Φ_c	Φ_1	Φ_7
0 (2.27)	0.28	0.011	0.0013
5 (2.54)	0.27	0.010	0.0013
10 (2.80)	0.26	0.0083	0.0014
40 (4.40)	0.27	0.0039	0.0015
60 (5.46)	0.26	0.0023	0.0015
100 (7.58)	0.28	0.0014	0.0016

[a] All solutions contained 1% pyridine and were irradiated at 334 nm. [b] Calculated assuming $\epsilon = \Sigma v_i \epsilon_i$.

Table II. Quantum Yields for Isomerization and Adduct Formation for 0.01 M *trans*-Stilbene in Benzene[a]

dimethyl fumarate, M	Φ_c	Φ_1	Φ_7
0	0.45	0	0
0.125	0.31	0.0080	0.0010
0.144	0.30	0.0086	0.0012
0.167	0.28	0.0094	0.0012
0.201	0.26	0.011	0.0013
0.251	0.25	0.014	0.0014
0.390	0.20	0.017	0.0013
∞		0.041[b]	

[a] See Table I, note *a*. [b] Extrapolated value; see text.

Table III. Quantum Yields for Isomerization and Adduct Formation for 0.10 M *trans*-Stilbene in Benzene[a]

dimethyl fumarate, M	Φ_c	Φ_1	Φ_7
0	0.44	0	0
0.126	0.33	0.0081	0.036
0.143	0.32	0.0090	0.036
0.168	0.29	0.0096	0.039
0.201	0.27	0.010	0.036
0.250	0.24	0.012	0.036
0.333	0.21	0.015	0.036
∞		0.037[b]	

[a,b] See notes to Table II.

Table IV. Quenching of *trans*-Stilbene Fluorescence by Electron-Poor Alkenes[a]

quencher	$E(A^-/A)$,[b] V	IP,[c] eV	$k_q\tau$, M^{-1}
fumaronitrile	−1.36	11.2	7.0
dimethyl maleate	−1.45	10.5	4.2
dimethyl fumarate	−1.54	10.7	7.6
dimethylisopropylidene malonate	−2.13		0.9[d]
acrylonitrile	−2.36	10.9	1.2
methyl acrylate		10.5	0.7
methyl methacrylate	−2.38	10.1	0.5
1,1-dichloroethylene		10.0	0.2
carbon tetrachloride	−0.25	11.5	1.8

[a] Nondegassed benzene solutions containing 10^{-4} M TS, λ_{ex} 320 or 330 nm. [b] Reduction potential in aprotic solvents. Most values (vs. Ag/Ag^+ in dimethylformamide) are from J. P. Petrovich, M. M. Baizer, and M. R. Ort. *J. Electrochem. Soc.*, **116**, 743 (1969). [c] Vertical ionization potentials from diverse sources. [d] Value was obtained from cycloaddition quantum yields.

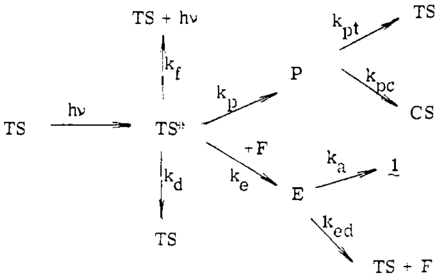
compatible with cyclobutane formation via a singlet exciplex in which secondary π-orbital overlap is maximized (vide infra). Further evidence for an exciplex intermediate is provided by the observation that fluorescence quenching of TS by F is accompanied by the appearance of a weak structureless emission with λ_{max} 505 ± 10 nm in benzene solution. The excitation spectrum of this emission is identical with that for *trans*-stilbene fluorescence; however, its lifetime (2 ± 1 ns by oxygen quenching[8]) is longer than that of singlet stilbene (0.1 ns).[9] Exciplex fluorescence from TS–F is solvent sensitive and cannot be detected in tetrahydrofuran (ϵ 7.58) or more polar solvents.

Quantum yields for TS isomerization (Φ_c) and formation of **1** and **7** in benzene–tetrahydrofuran mixed solvent are given in Table I. Values of Φ_c and Φ_7 are insensitive to solvent; however, Φ_1 decreases markedly with increasing solvent polarity. This decrease parallels the decrease in exciplex fluorescence intensity and indicates that **1**, but not **7** or CS, is formed from the TS–F exciplex. The dependence of quantum yields on the concentration of F at constant TS concentration (Tables II, III) supports this conclusion. The value of Φ_1 increases with [F], as expected for exciplex cycloaddition; however, Φ_7 is independent of [F]. Ignoring for the moment the formation of **7**, a simplified mechanism for formation of **1** via an exciplex intermediate (E) is given in Scheme I, where P is a twisted or perpendicular stilbene singlet which can decay to either TS or CS.[7] According to this scheme, Stern–Volmer expressions for cycloaddition and quenching of fluorescence and CS formation are given by eq 1 and 2.

$$\frac{1}{\Phi_1} = \frac{k_a + k_{ed}}{k_a}\left(1 + \frac{k_f + k_d + k_p}{k_e[F]}\right) \qquad (1)$$

$$\frac{\Phi_f^\circ}{\Phi_f} = \frac{\Phi_c^\circ}{\Phi_c} = 1 + \frac{k_e[F]}{k_f + k_d + k_p} \qquad (2)$$

Scheme I



Plots of Φ_1^{-1} vs $[F]^{-1}$ and Φ_c°/Φ_c vs. [F] for the data in Tables II and III are linear as required by Scheme I. The limiting values of Φ_1 (0.041, 0.037) are low, indicating that cycloaddition is a minor exciplex decay pathway. Values of the Stern–Volmer quenching constant $k_{SV} = k_e\tau$ ($\tau^{-1} = k_f + k_d + k_p$) for formation of **1** (k_{SV} = 1.9 for 0.01 M TS, k_{SV} = 3.3 for 0.1 M TS) and quenching of CS formation (K_{SV} = 3.0 for 0.01 M TS, k_{SV} = 3.8 for 0.1 M TS) are in reasonable agreement. The value of k_{SV} obtained from fluorescence quenching of 10^{-4} M TS in benzene solution is somewhat higher (Table IV). This disagreement may reflect several complications of the kinetics (e.g., reversible stilbene twisting,[9] ground-state complexation, stilbene excimer formation) which will be considered subsequently.

One possible complication of the kinetic analysis is the formation of a weak ground-state complex between TS and F. The ultraviolet absorption spectra of TS–F mixtures are nonadditive at high concentrations, the onset of absorption being distinctly red shifted. The equilibrium constant for complexation is estimated to be 1.0 ± 0.5 from electronic absorption spectra[10a] and 1.3 ± 0.2 from ^{13}C chemical shifts.[10b] Irradiation of TS (0.11 M) and F (0.42 M) at 365 nm selectively excites the ground-state complex (<5% absorption by TS), while irradiation at 334 nm selectively excites TS (>90% absorption by TS). The product quantum yields for 334-nm excitation (Table V) are similar to those given in Table III for comparable concentrations. Irradiation at 365 nm gives a higher Φ_1 and lower Φ_c and Φ_7 values, results strikingly similar

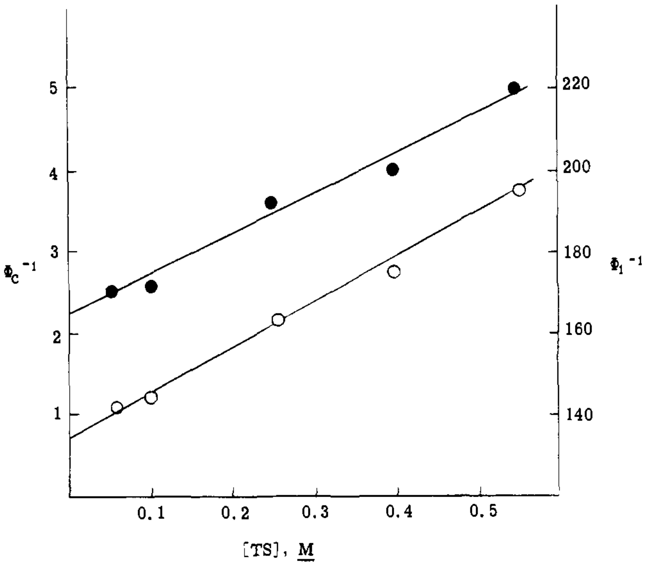


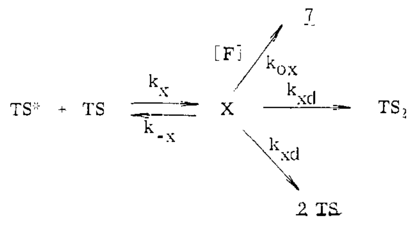
Figure 1. Dependence of the quantum yields for formation of dimethyl μ-truxinate (Φ_1, ○) and *cis*-stilbene (Φ_c, ●) upon *trans*-stilbene concentration with least-squares fit.

Table V. Wavelength Dependence of Quantum Yields[a,b]

λ, nm[c]	Φ_c	Φ_1	Φ_3
334	0.16	0.018	0.035
365	0.04	0.035	0.012

[a] Degassed benzene solutions containing 0.11 M *trans*-stilbene and 0.42 M dimethyl fumarate. [b] See notes for Table I. [c] Wavelength of irradiation.

Scheme II



to those obtained for dilute TS at high concentrations of F. Under these conditions, all singlet TS would be quenched by F to form exciplex. *Thus excitation of the weak ground-state complex produces an excited species which displays the same chemical behavior as the exciplex.* Further evidence for the identity of exciplex and excited-ground-state complex is provided by the observation of long wavelength fluorescence (but not TS fluorescence) when 0.12 M TS and 0.43 M F are excited in the charge-transfer absorption band (360 nm). Both the spectral distribution and lifetime of this emission are identical with those obtained for the TS-F exciplex. The inefficient formation of CS from the TS-F exciplex will be discussed in a subsequent publication.

Returning to the formation of oxetane **7**, the dependence of its formation upon TS concentration noted in the preparative experiments is confirmed by the quantum yield measurements given in Table VI. The only satisfactory explanation of the TS concentration dependence of Φ_7 is that stilbene excimer (X) reacts with F to form**7** (Scheme II). Stilbene excimer fluorescence has been observed following γ irradiation of TS in a squalene glass at 77 K,[11] but cannot be detected at room temperature in solution, presumably owing to efficient formation of stilbene dimer (TS_2).[12] Self-quenching of stilbene fluorescence, isomerization (Φ_c) and cyclobutane formation (Φ_1) are all readily observable at TS concentrations above 10^{-1} M (Table VI).

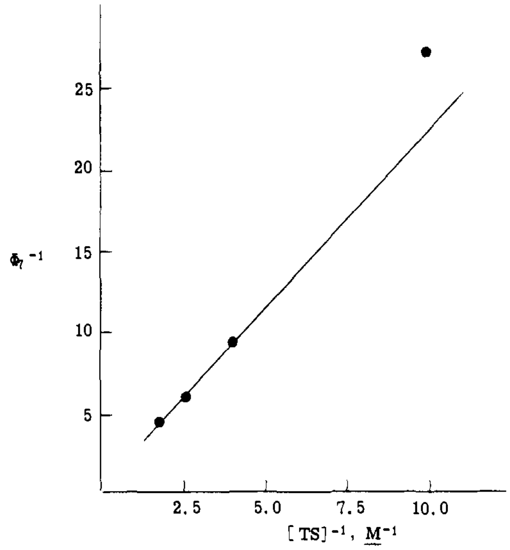


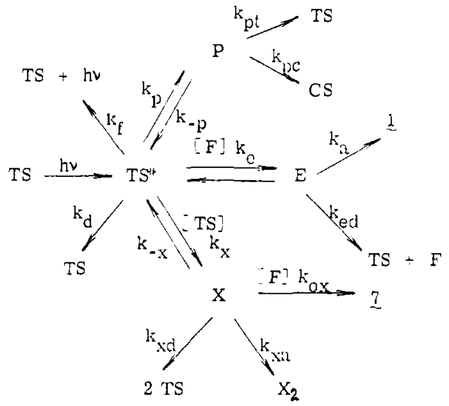
Figure 2. Dependence of the quantum yield for formation of oxetane (Φ_7) upon *trans*-stilbene concentration with least-squares fit to high concentration values.

Table VI. *trans*-Stilbene Concentration Dependence of Quantum Yields[a,b]

trans-stilbene, M	Φ_c	Φ_1	Φ_7
0.010	0.35	0.0069	0.0017
0.050	0.39	0.0070	0.014
0.10	0.38	0.0069	0.037
0.25	0.28	0.0057	0.11
0.40	0.25	0.0061	0.17
0.55	0.20	0.0051	0.24

[a] See Table I, note *a*. [b] 0.1 M dimethyl fumarate.

Scheme III



Concurrent operation of Schemes I and II yields Scheme III. Expressions for the concentration dependence of Φ_1 (eq 3), Φ_c (eq 4), and Φ_7 (eq 5) have been derived using the simplifying assumptions of irreversible exciplex formation[13] and no quenching of twisted stilbene (P). Plots of Φ_1^{-1} and Φ_c^{-1} vs. [TS] at constant [F] are shown in Figure 1 and are linear as required by the proposed mechanism. A plot of Φ_7^{-1} vs. $[TS]^{-1}$ (Figure 2) is linear for high stilbene concentrations. Deviations from linearity at low stilbene concentrations are within the experimental error for simultaneous measurement of high and low quantum yields. It should be noted that eq 3–5 were derived for analysis of data obtained at constant [F] and that γ is dependent upon [F]. The lack of dependence of Φ_7 upon [F] at constant [TS] (Tables II, III) is consistent with the appearance of [F] in both the numerator and denominator of eq 5 and is a consequence of the competition between ex-

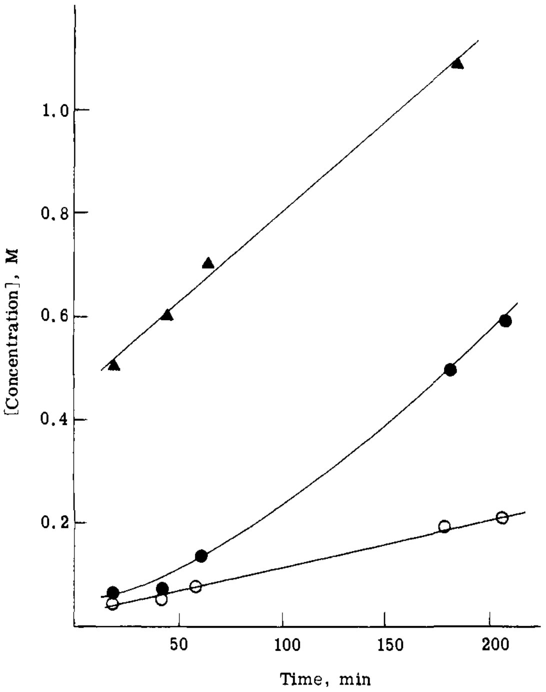


Figure 3. Conversion of *cis*-stilbene to *trans*-stilbene (▲, × 10^{-3} M) and truxinates **4** (○, × 10^{-4} M) and **1** (●, × 10^{-4} M).

cimer and exciplex formation. Equation 3 reduces to the form of eq 1 at low [TS]. A more complete kinetic analysis of the available data must await measurement of the stilbene excimer lifetime.

$$\frac{1}{\Phi_1} = \frac{k_d + k_f + k_p(1 - k_{-p}\tau_p) + k_x[\mathrm{TS}](1 - k_{-x}\gamma)}{\tau_E k_e k_a[\mathrm{F}]} + (\tau_E k_a)^{-1} \quad (3)$$

$$\frac{1}{\Phi_c} = \frac{k_d + k_f + k_e[\mathrm{F}] + k_x[\mathrm{TS}](1 - k_{-x}\gamma)}{k_{pc}\tau_P k_p} + \frac{1 - k_{-p}\tau_P}{k_{pc}\tau_P} \quad (4)$$

$$\frac{1}{\Phi_7} = \frac{k_d + k_f + k_e[\mathrm{F}] + k_p(1 - k_{-p}\tau_P)}{k_{ox}\gamma k_x[\mathrm{TS}][\mathrm{F}]} + \frac{1 - k_{-x}\gamma}{k_{ox}\gamma[\mathrm{F}]} \quad (5)$$

$$\tau_P^{-1} = k_{-p} + k_{pt} + k_{pc}$$

$$\tau_E^{-1} = k_a + k_{ed}$$

$$\gamma^{-1} = k_{ox}[\mathrm{F}] + k_{xd} + k_{xa} + k_{-x}$$

***cis*-Stilbene–Dimethyl Fumarate.** The formation of dimethyl *neo*-truxinate (**4**) as a minor product in the preparative photolysis of TS and F suggested the possibility of a nonconcerted pathway for the cycloaddition process.[14] Such a nonconcerted pathway was also proposed by Rosenberg and Servé[15] for the addition of TS and CS to 2-methyl-4,5-dihydrofuran. Our results establish that **4** is not a primary product of the TS–F reaction and that **1** is not isomerized to **4** under the reaction conditions. Since **4** is formally the product of concerted addition of CS with F, an investigation of this reaction was undertaken.

Direct photolysis of CS is known to yield TS ($\Phi = 0.35$) and dihydrophenanthrene ($\Phi = 0.10$).[16] Neither of these reactions is perceptibly (>5%) quenched by 0.30 M F in benzene solution at 25 °C. The only products observed by GC analysis at low conversions of CS are TS and the truxinates **1** and **4** (Figure 3). The ratio of **4**:**1** decreases with CS conversion, having a maximum value of 0.8 at the lowest conversion (~2%). This ratio is also dependent upon the initial purity of the CS, decreasing with increasing TS concentration. These results indicate that **4** is formed from a highly inefficient reaction of CS with F. The quantum yield for this reaction is estimated to be 3×10^{-3} from a comparison of the yields of **4** and TS at low conversion (Figure 3). The low quantum yield for this reaction is consistent with the failure to observe quenching of CS isomerization or dihydrophenanthrene formation by F. The rate of thermal (dark) decay of dihydrophenanthrene absorption is 2.8 times faster in the presence of 0.10 M F than in its absence at 23 °C. Accelerated thermal decay is not accompanied by formation of **4**. Electron-poor alkenes have recently been reported to oxidize dihydrophenanthrene to phenanthrene.[17] Oxidation of dihydrophenanthrene by F could account for the observed acceleration of thermal decay.

***trans*-Stilbene–Dimethyl Maleate (M).** Preparative photolysis of TS with M proceeds more slowly and yields a more complex product mixture than is the case for photolysis of TS with F. The major isolated product is truxinate **3**, obtained along with lesser amounts of **1**, **2**, and stilbene dimers. Irradiation of 0.030 M TS and 0.50 M M gave only CS and **3** by GC analysis at TS conversions <10%. Fluorescence quenching of TS by M gives a lower k_{SV} than does quenching by F (Table IV) and is not accompanied by detectable exciplex fluorescence.

Reaction of singlet CS and dimethyl maleate could, in principle, give the only missing member of the truxinate series, ω-**6** along with the known β-truxinate (**5**). Unfortunately, the efficient isomerization of CS to TS precludes meaningful preparative bimolecular reactions of CS. The absence of an authentic source of **6** further precludes low conversion gc analysis.

Other Electron-Poor Alkenes. Values of k_{SV} for quenching of TS by several electron-poor alkenes and carbon tetrachloride are included in Table IV. Exciplex fluorescence was observed only for quenching by F and fumaronitrile (FN). The TS–FN exciplex fluorescence maximum and lifetime (8 ns by single photon counting) are the same for excitation of dilute (2.5×10^{-4} M) TS at 330 nm and concentrated (0.12 M) TS at 390 nm. Thus the physical behavior of the excited charge-transfer complex is the same as that of the exciplex. Both the long exciplex lifetime (relative to singlet TS) and the increase in the exciplex:monomer fluorescence intensity ratio with increasing temperature (Figure 4) indicate that exciplex formation is irreversible. Exciplex fluorescence is red shifted (λ_{max} 550 ± 5 vs. 504 ± 5 nm), greatly diminished in intensity in tetrahydrofuran vs. benzene solution, and cannot be detected in more polar solvents.

Cycloadduct formation was observed for TS with several of the weaker electron acceptors including dimethylisopropylidene malonate, acrylonitrile, methyl cinnamate, and crotonic acid. The quantitative aspects of these reactions have not been investigated. No adducts were observed for the stronger electron acceptors fumaronitrile, maleic anhydride, and tetracyanoethylene. Formation of CS from the TS–FN and TS–maleic anhydride exciplexes will be discussed in a subsequent publication. Irradiation of TS with maleic anhydride in benzene solution produces homodimers of TS and maleic anhydride, whereas irradiation in polar solvents yields the alternating copolymer.[20] Irradiation of the strong ground-state complex between TS and tetracyanoethylene ($K = 23$, λ_{max} 595 nm)[19] at 580 nm results in neither adduct formation nor TS isomerization. Prolonged irradiation at 313 nm results in formation of phenanthrene, presumably owing to oxidation of dihydrophenanthrene by tetracyanoethylene.[17]

The quenching constants given in Table IV increase with increased alkene electron affinity, as measured by either reduction potential in nonaqueous solution or gas phase ionization potential.[21] The free energy for electron transfer from singlet stilbene to ground-state alkene can be estimated using

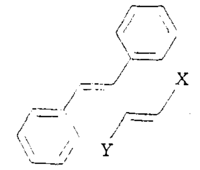
$$\Delta G = E(\mathrm{D/D^+}) - E_s - E(\mathrm{A^-/A}) - \mathrm{const} \qquad (6)$$

where $E(\mathrm{D/D^+})$ is the stilbene oxidation potential (1.50 V vs. SCE in acetonitrile[22]), E_s is the stilbene singlet energy (3.53 eV), $E(\mathrm{A^-/A})$ is the alkene reduction potential, and the constant term is the energy required to bring the radical ions to the encounter distance.[23] The formation of a charge-transfer stabilized exciplex should be most favorable for alkenes with $E(\mathrm{A^-/A}) < -2.0$ V, in accord with the results in Table IV. Calculation of the actual quenching rate constants is complicated by the formation of ground state complexes with the stronger acceptors.

Summary and Conclusions

The cycloaddition reactions of singlet TS with dimethyl fumarate and maleate proceed with retention of TS and alkene stereochemistry as is the case for TS addition with electron-rich alkenes.[3,4] Retention of stereochemistry is also inferred for the highly inefficient addition of CS to F. These results suggest that the planar TS and CS singlet states react in a concerted or quasi-concerted fashion with alkenes, but that the twisted singlet state(s) of stilbene fails to form cycloadducts. The failure of triplet stilbene to react with electron-rich or electron-poor alkenes may also reflect the unreactive nature of the twisted triplet state. The efficiency of cycloaddition thus parallels the lifetime of the planar stilbene excited state, which is in turn determined by the rate of twisting about the central double bond.[7] Both singlet and triplet cycloaddition reactions have been observed for molecules in which CS is incorporated into a small-ring system,[3b,4] thus prolonging the lifetime of the planar excited state.

The necessity of a planar stilbene excited state for alkene addition is consistent with an exciplex mechanism (Schemes I, III). The normal sandwich-type exciplex geometry[23b] with optimum π-orbital overlap can be attained only with a planar stilbene excited state. Secondary overlap between phenyl and carbomethoxy groups can account for the orientational selectivity of cycloaddition with F (**1** ≫ **2**). A lesser degree of orientational selectivity is observed when only one alkene substituent (X or Y) possesses π electrons.[3] A further indication of the importance of π-orbital overlap in stilbene exciplex formation is provided by a comparison of TS quenching by alkenes vs. carbon tetrachloride[24a] (Table IV). Carbon tetrachloride is a stronger electron acceptor than any of the alkenes in Table IV and is known to form weak ground-state complexes with aromatic hydrocarbons;[24b] yet the observed quenching constant is less than that for several of the alkenes. A similar situation was encountered in the comparison of π donors (2,5-dimethyl-2,4-hexadiene IP = 7.8 eV, $k_{SV} = 4.5$ M^{-1}) vs. σ donors (trimethylamine IP = 7.8 eV, $k_{SV} = 1.6$ M^{-1}).[5] Chemically reactive π-donor and -acceptor exciplexes may be formed less reversibly than unreactive trialkylamine or carbon tetrachloride exciplexes, thus accounting for the larger observed quenching constants.[3c,5]



The reactions of TS with strong electron acceptors ($E(\mathrm{A^-/A}) < -2$ V) are characterized by rapid and irreversible quenching and inefficient cycloaddition. Quantum yields for cycloadduct formation decrease as the polarity of the exciplex is increased, either by using a stronger acceptor or a more polar solvent. We have previously observed that rate constants for exciplex cycloaddition decrease with increasing solvent polarity, presumably owing to greater solvent stabilization of the polar exciplex than the transition state leading to nonpolar cycloadducts.[3c] Further investigations of the nonradiative decay processes of these highly polar exciplexes are in progress.

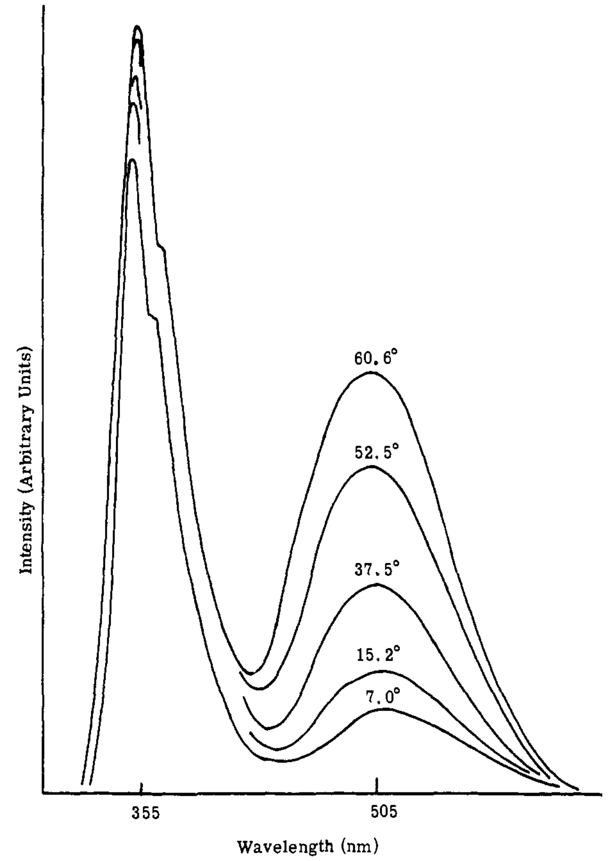
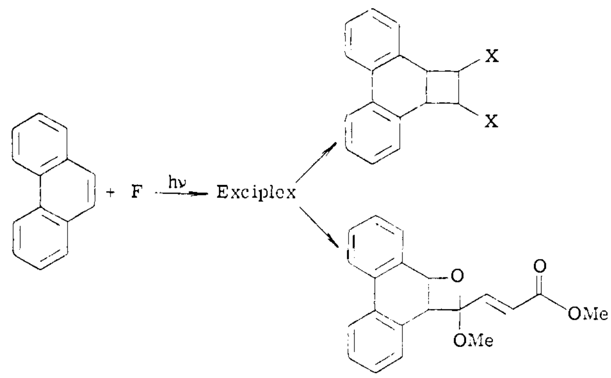


Figure 4. Emission spectra of *trans*-stilbene (2.5 × 10^{-4} M) and fumaronitrile (0.3 M) in benzene solution as a function of temperature.

Weak ground-state complexes are formed between TS and the electron-poor alkenes F and FN. Excitation of the ground-state complex results in the same chemical reactions and fluorescence which are observed for the exciplexes formed upon diffusive encounter of excited TS and ground-state alkene. Thus the same excited-state complex must be formed in both processes, either directly or by rapid relaxation of the initially formed excited state. The opposite result has been reported for the reaction of acenaphthylene with tetracyanoethylene.[25] Excitation of uncomplexed acenaphthylene results in cycloaddition, whereas excitation of the ground-state complex does not. There are also several reports of different emission from excited ground-state complexes and complexes formed upon diffusive encounter of the same pair of molecules.[26] It is possible that geometry differences may be responsible for these observations.

Oxetane formation is a common reaction of electronically excited carbonyl compounds.[27] The only previous example of cycloaddition to a ground-state carbonyl is that of singlet and triplet phenanthrene to F.[28] These reactions yield cyclobutanes as well as oxetane and have been shown to proceed via a common exciplex intermediate (eq. 7). A common exciplex intermediate for formation of cyclobutane and oxetane from TS and F has been ruled out on the basis of the concentration and solvent dependence of the quantum yields. The formation of oxetane via quenching of the TS excimer has important implications for mechanistic and preparative photochemistry. Many excimers and exciplexes have sufficiently long lifetimes



(7)

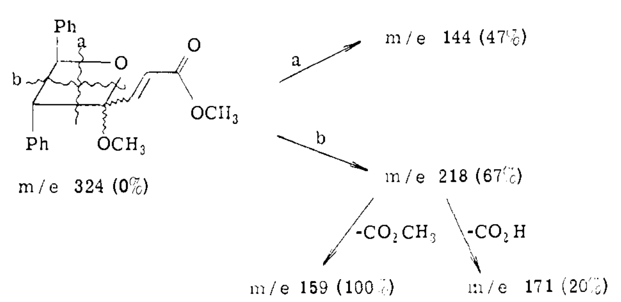
to allow interception by a third molecule.[29-33] Amines and dienes are known to enhance the photodimerization of anthracene[32,33] and the inefficient cycloaddition of coumarin and tetramethylethylene apparently involves interception of the coumarin excimer.[34] However, we are unaware of any previous examples of different chemical reactions resulting from interception of an excimer vs. a monomer. Electronic and geometric requirements of exciplex quenching have recently been described and rationalized using a frontier molecular orbital approach by Caldwell and co-workers.[30c,d] These requirements should prove useful in the design of future investigations of the scope and synthetic utility of termolecular photochemical reactions.

Experimental Section

General Procedures. *trans*-Stilbene (Aldrich) was recrystallized twice from benzene-hexane and twice from absolute ethanol. *cis*-Stilbene (Aldrich) was chromatographed on neutral alumina (pentane elutant), distilled under vacuum and contained 0.2% trans impurity by GC analysis. The trans impurity increased on exposure to room light; so care was taken to conduct all manipulations and analyses in a dark room. Dimethyl fumarate (Eastman) and fumaronitrile (Aldrich) were recrystallized three times from benzene-hexane and contained <0.5% isomeric impurity by GC analysis. Dimethyl maleate, methyl acrylate, methyl methacrylate, and acrylonitrile were fractionally distilled prior to use. Spectroquality benzene (Aldrich) was refluxed over two successive portions of phosphorus pentoxides and distilled. Spectroquality hexane (Aldrich) was successively distilled from sulfuric acid, potassium carbonate, and phosphorus pentoxide. Other solvents were purified by standard techniques.

Preparative photolyses were carried out under a nitrogen atmosphere using a Hanovia 450-W medium-pressure mercury lamp in a water-cooled Pyrex lamp well. Quantum yields were determined on degassed samples contained in sealed 15-mm-o.d. Pyrex test tubes maintained at 25 ± 2 °C. Monochromatic 313- and 365-nm irradiation was provided by a potassium chromate solution and Corning 7-54 and 0-52 filters, respectively. Other spectral lines (334, 390, 595 nm) were isolated with a Bausch and Lomb high intensity 0.25-m monochromator. Light intensities were determined using benzophenone-benzhydrol and potassium ferrioxylate actinometers. Solutions were analyzed for product formation with a dual flame ionization gas chromatograph using a 6 ft × 1/8 in. column containing 5% SF-96 on Chromosorb G (for cycloadduct) or a 8 ft × 1/8 in. column containing 20% Carbowax 20M on Chromosorb P (for isomerized alkenes). Ultraviolet absorption spectra were recorded using a GCA/McPhearson EU-700 spectrophotometer, fluorescence spectra using a Hitachi-Perkin-Elmer MPF-2A spectrophotometer, infrared spectra using a Beckman IR-5 spectrophotometer, NMR spectra using a Perkin-Elmer R20B spectrometer, and mass spectra using a Hewlett-Packard 5930A mass spectrometer.

Addition of *trans*-Stilbene to Dimethyl Fumarate. The isolation and characterization of **1**, **2**, and **4** from the preparative photolysis of TS (0.028 M) and F (0.28 M) in benzene has previously been described.[14] TS (3.60 g, 0.020 mol) and F(3.17 g, 0.022 mol) in 3:2 benzene-tetrahydrofuran containing 2% pyridine were irradiated for 36 h. The solvent was removed under vacuum and the residue chromatographed on 1000 g of Merck silica gel using ethyl acetate in hexane. Unreacted stilbenes and phenanthrene were eluted with 2% ethyl acetate. Elution with 5% ethyl acetate provided a mixture of oxetanes **7** and **8** (0.50 g, 8%) followed by pure **7** (0.61 g, 9%). Recrystallization of **7** from methanol yielded white needles, mp 71-72°. The NMR displayed vinyl doublets at δ 6.39 and 7.54 (J = 15.7 Hz), broadened cyclobutane methine singlets at 3.75 and 6.17, methoxy singlets at 3.75 and 3.78, and an aromatic multiplet centered at 7.30. The mass spectrum showed the expected oxetane retro-[2 + 2] reactions to give benzaldehyde and stilbene fragments along with the loss of CO_2H and CO_2CH_3 expected for an α,β-unsaturated ester.[35] Anal. Calcd for $C_{20}H_{20}O_4$: C, 74.05; H, 6.22. Found: C, 74.20; H, 6.05. Continued elution with 10% ethyl acetate gave **1** (1.23 g, 19%) and **4** (0.22 g, 3%), identified by comparisons with authentic samples.[14]



Compound **9** was isolated, as described,[14] from preparative irradiations not containing pyridine and crystallized from methylene chloride-methanol: mp 218-220 °C; NMR δ ($CDCl_3$) 3.00, 3.33, 3.72, 3.77 (4 × 3 H, s's, OCH_3), 3.68-4.21 (3 H, m, cyclobutane), 6.09, 7.04 (2 × 1 H, J = 16 Hz, vinyl doublets), 7.25 (5 H, m, Ph). The mass spectrum displayed a molecular ion (*m/e* 362) and peaks due to loss of dimethyl fumarate (218) and methyl cinnamate (218) fragments. Anal. Calcd for $C_{19}H_{22}O_7$: C, 62.98; H, 6.07. Found: C, 62.30; H, 6.09.

Addition of *trans*-Stilbene to Dimethyl Maleate. A solution of TS (5.0 g, 0.028 mol) and M (80.0 g, 0.55 mol) in 600 mL of benzene was irradiated under nitrogen for 24 h. After removal of solvent and unreacted starting materials under vacuum, the residue, 4.8 g, was chromatographed on 150 g of Merck silica gel using ethyl acetate in hexane. Residual stilbene and stilbene dimers were eluted with 2% ethyl acetate. Elution with 5% ethyl acetate afforded **1** (0.19 g, 2.1%), a mixture of **1** and **3** (0.14 g, 1.5%), and impure **3** (0.62 g, 6.9%). Recrystallization of **3** from ethanol gave 0.16 g of pure material: mp 116-118 °C (lit.[36] mp 116 °C); δ ($CDCl_3$) 3.30, 3.73 (3 H, 3 H, s, OCH_3), 3.8-4.2, 4.5-4.9 (4 H, m, cyclobutane hydrogens), 7.28 (10 H, m, aromatic hydrogens). Further elution afforded yellow oily mixtures whose NMR spectra showed aromatic and carbomethoxy absorption.

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Electron Transfer Processes. 20. Conversion to *p,p'*-Dinitrostilbene and Other Examples of the $S_{RN}1$ Substitution Reactions of *p*-Nitrobenzyl Derivatives

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Abstract: The following reactions have been demonstrated to proceed by electron-transfer mechanisms and to involve intermediate radicals and radical anions: (a) the coupling of the anion of 2-nitropropane with *N*-(*p*-nitrobenzyl)pyridinium chloride to form 2-nitro-2-methyl-1-(*p*-nitrophenyl)propane; (b) the coupling of the anion of 2-nitropropane with *p*-nitro-α,α-dimethylbenzyl phenyl sulfoxide or sulfone to yield 2-nitro-3-(*p*-nitrophenyl)-2,3-dimethylbutane; (c) the base-catalyzed coupling of *p*-nitrobenzyl chloride or dimethyl-*p*-nitrobenzylsulfonium bromide to give *p,p'*-dinitrostilbene; (d) the substitution reaction of thiophenoxide ion with *p*-nitro-α,α-dimethylbenzyl phenyl sulfoxide or sulfone to yield *p*-nitro-α,α-dimethylbenzyl phenyl sulfide.

It is recognized that numerous reactions of *p*-nitrobenzyl derivatives proceed by free-radical and/or radical-anion intermediates. It has been demonstrated by ESR spectroscopy that a wide variety of carbanions will transfer an electron to nitrobenzenes or nitroalkanes:[1-3]

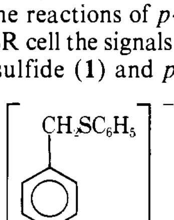
$$R:^- + R'NO_2 \rightarrow R\cdot + [R'NO_2]^-\cdot \qquad (1)$$

Reaction 1 has been shown to be involved in the spontaneous disproportionation of *p*-nitrotoluene,[2-4] in the autoxidation of 2-nitropropane or *p*-nitrotoluene in basic solutions,[5,6] in the oxidation of fluorene anion catalyzed by nitroaromatics,[7] in the C-alkylation of the anion of 2-nitropropane by 2-halo-2-nitropropanes,[8] *p*-nitrobenzyl chloride,[8-9] *p*-nitrobenzyldimethyl sulfonium salts,[8] *p*-nitro-α,α-dimethylbenzyl chloride,[10] α,*p*-dinitrocumene,[11] *p*-nitrobenzyl pentachlorobenzoate,[9] and undoubtedly trimethyl-*p*-nitrobenzylammonium salts,[8-12] in the oxidative dimerization by nitroaromatics or 2-chloro-2-nitropropane of the anions of indoxyl,[13] 1,3-dithianes,[14,15] diphenylacetonitrile[15] or ω,ω-di(methylmercapto)acetophenone,[15] and other benzylic or allylic anions.[15]

We now report some other examples of a radical chain process involving the *p*-nitrobenzyl moiety including (a) the base-catalyzed reaction of *p*-nitrobenzyl sulfonium salts or *p*-nitrobenzyl chloride to yield the *p,p'*-dinitrostilbene, (b) the substitution reactions of *N*-(*p*-nitrobenzyl)pyridinium chloride and *p*-nitro-α,α-dimethylbenzyl phenyl sulfoxide and sulfone with the anions of 2-nitropropane or thiophenol.

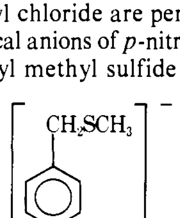
Results and Discussion

Reaction of *p*-Nitrobenzyl Chloride with Mercaptide Ion. The reaction on thiophenoxide or methyl mercaptide[16] ions with *p*-nitrobenzyl chloride in ethanol yields the corresponding *p*-nitrobenzyl sulfides (in 97 and 68% yields, respectively). When the reactions of *p*-nitrobenzyl chloride are performed in an ESR cell the signals of the radical anions of *p*-nitrobenzyl phenyl sulfide (**1**) and *p*-nitrobenzyl methyl sulfide (**2**) are



1

$a^N = 12.60$ G
$a_{3,5}{}^H = 3.48$ G
$a_{2,6}{}^H = 2.25$ G
$a_{CH_2}{}^H = 0.9$ G



2

$a^N = 12.50$ G
$a_{3,5}{}^H = 3.5$ G
$a_{2,6}{}^H = 2.2$ G
$a_{CH_2}{}^H = 1.0$ G

readily detected. Radical ions **1** and **2** are also formed when the performed sulfides are treated with the mercaptide ions in ethanol. The reaction of thiophenoxide ion with *p*-nitrobenzyl chloride at 0 °C in ethanol was not significantly retarded by 10 mol % of *p*-dinitrobenzene or significantly accelerated by

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