

# Formation and Reactions of Stilbene Exciplexes

FREDERICK D. LEWIS

Department of Chemistry, Northwestern University, Evanston, Illinois 60201

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Both the electron-donor and electron-acceptor properties of organic molecules are enhanced by electronic excitation. The energy required to remove an electron from an excited donor ( $D^*$ ) approximately equals the ionization potential minus the excitation energy ( $IP - E_S$ ). Similarly the energy gained upon adding an electron to an excited acceptor ( $A^*$ ) equals the electron affinity plus the excitation energy ( $EA + E_S$ ). As a consequence of the enhanced donor and acceptor properties of organic molecules in their excited states, excited-state complexes are obtained from donor-acceptor pairs which do not form stable ground-state complexes. The study of excited-state dimers (excimers) and complexes (exciplexes) has been a fertile area of investigation since Förster's<sup>1</sup> observation of excimer fluorescence in 1954 and Weller's<sup>2</sup> observation of perylene-*N,N*-dimethylaniline exciplex fluorescence in 1963. The photophysics of inter- and intramolecular complexation and decay has been elucidated for a large number of excimers and exciplexes, mostly those of aromatic hydrocarbons.<sup>3</sup>

The possible intermediacy of an "oriented  $\pi$  complex" in a bimolecular photochemical reaction was first advanced in 1964 by Corey<sup>4</sup> in order to rationalize the regioselectivity of triplet enone-olefin cycloaddition. It subsequently became fashionable to attribute the vagaries of photochemical addition reactions to exciplex intermediates.<sup>5</sup> However, the connection between exciplex photophysics and photochemistry remained suspect until 1974 when Caldwell<sup>6</sup> demonstrated that both cycloaddition and exciplex fluorescence from the 9-cyanophenanthrene-anethole exciplex were quenched to the same extent by a third molecule, dimethyl acetylenedicarboxylate. Since quenching of 9-cyanophenanthrene monomer fluorescence was less efficient, the fluorescent exciplex became, perforce, an intermediate in the cycloaddition process. Concurrent and subsequent investigations in several laboratories have firmly established the intermediacy of exciplexes<sup>7-12</sup> and excimers<sup>13-15</sup> in a large number of bimolecular photochemical reactions.

During the past several years the chemical and physical behavior of the singlet-state exciplexes formed between *trans*-stilbene with several classes of ground-state molecules (amines,<sup>16</sup> electron-poor<sup>17</sup> and electron-rich alkenes,<sup>18</sup> and dienes<sup>19</sup>) has been investigated in this laboratory. While other exciplex systems have been investigated in greater detail, the stilbene exciplexes are unique in the variety of addition products they afford and the information they provide about the

fundamental nature of photoaddition processes. In view of the important role of the unimolecular reactions of the stilbenes (*cis*  $\rightleftharpoons$  *trans* isomerization<sup>20</sup> and *cis*-stilbene  $\rightleftharpoons$  dihydrophenanthrene interconversion<sup>21</sup>) in the development of mechanistic and synthetic photochemistry, it is perhaps fitting that the bimolecular reactions of *trans*-stilbene should provide the subject of this Account.

## Background

A rudimentary introduction to exciplex formation and decay will suffice for the purposes of this Account. By analogy to Mulliken's<sup>22</sup> description of ground-state charge-transfer complexes, an exciplex can be described as a resonance hybrid of locally excited and charge-transfer configurations (eq 1).<sup>23</sup> Potential-energy

$$\Psi(AD)^* = a\Psi(A^*D) + b\Psi(A^{\cdot-}D^{\cdot+}) \quad (1)$$

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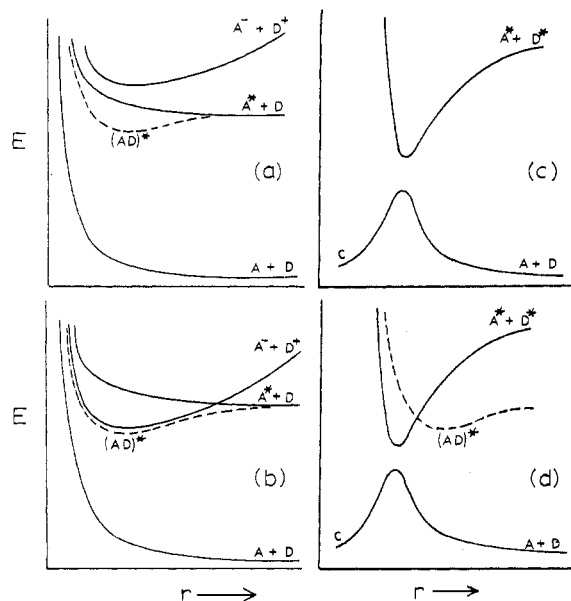
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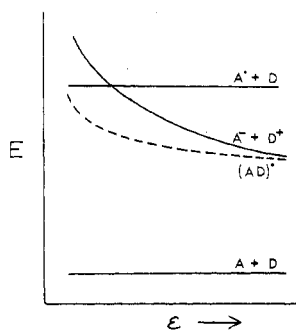
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Frederick D. Lewis was born in Boston, MA, and received his B.A. degree from Amherst College in 1965. After receiving the Ph.D. degree from the University of Rochester (with W. H. Saunders, Jr.) and postdoctoral work at Columbia University (with N. J. Turro), he joined the faculty at Northwestern University, where he is now Associate Professor of Chemistry. His research interests span the photochemical field from synthetic organic and organometallic photochemistry to photophysics and multiphoton infrared photochemistry.



**Figure 1.** Potential energy surfaces for (a) nonpolar exciplex, (b) polar exciplex, (c) [2 + 2] cycloaddition, and (d) exciplex cycloaddition.



**Figure 2.** Dependence of the exciplex potential energy on solvent dielectric constant.

surfaces for hypothetical nonpolar ( $a > b$ ) and polar ( $b > a$ ) exciplexes are shown in Figure 1a,b. The energy of the charge-transfer configuration is related to the free energy for electron transfer, which can be estimated from the electronic excitation energy and the electron affinity and ionization potential of the acceptor and donor (eq 2a) or, more commonly, their redox potentials

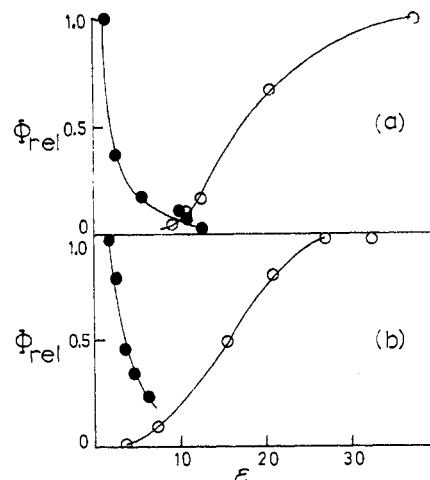
$$\Delta G_{ET} = E_S + EA_A - IP_D + \text{constant} \quad (2a)$$

$$= E_S + E_{(D/D^+)} - E_{A/A^-} + \text{constant} \quad (2b)$$

(eq 2b).<sup>24</sup> The energy of the charge-transfer configuration, and hence the exciplex, is highly dependent upon the solvent polarity as shown schematically in Figure 2.<sup>25</sup> Exciplex dipole moments ( $\mu$ ) can, in fact, be estimated from the solvent dependence of the exciplex fluorescence emission maximum ( $\nu$ ) using eq 3,

$$\bar{\nu} = \bar{\nu}_0 - \frac{2\mu^2}{hca^3} \left[ \frac{\epsilon - 1}{2\epsilon + 1} - \frac{n^2 - 1}{4n^2 + 2} \right] \quad (3)$$

where  $h$  is Planck's constant,  $c$  is the velocity of light,  $a$  is the solvent cavity radius (assumed to be  $\sim 4\text{--}5 \text{ \AA}$ ), and  $\epsilon$  and  $n$  are the solvent dielectric constant and index of refraction.<sup>26</sup> Values obtained for several aromatic



**Figure 3.** (a) Relative yields of fluorescence (●) and radical ions (○) from the pyrene-dimethylaniline exciplex and (b) relative yields of fluorescence (●) and addition (○) from the stilbene-triethylamine exciplex vs. solvent dielectric constant.

hydrocarbon-amine exciplexes using eq 3 (12–15 D)<sup>3b,27</sup> are higher than those from very recent electrooptical measurements (6–10 D).<sup>28</sup> However, eq 3 can be employed to obtain the relative dipole moments for a series of related exciplexes.

Polar exciplexes are known to dissociate into non-fluorescent radical ions in polar solvents.<sup>29</sup> Figure 3a shows the solvent dependence of the pyrene-dimethylaniline exciplex fluorescence<sup>30</sup> and radical ion formation.<sup>29</sup> As we shall see, dissociation into radical ions can have a profound effect on exciplex chemistry. Figure 3a also serves to illustrate the point that exciplex fluorescence may not be observed when efficient nonradiative decay pathways are operative. Since the fluorescence rate constants for aromatic hydrocarbon exciplexes are generally  $10^6\text{--}10^7 \text{ s}^{-1}$ ,<sup>3b</sup> an exciplex lifetime of 1 ns or longer may be necessary for the observation of exciplex fluorescence.

### Amine Addition Reactions

The chemical reactions of singlet *trans*-stilbene (TS) with simple alkylamines<sup>16</sup> serve to illustrate several important aspects of exciplex chemistry. Stilbene does not form products with simple tertiary amines in nonpolar solvents. In polar solvents addition of the amine  $\alpha\text{-C-H}$  bond occurs, accompanied by the formation of diphenylethane and tetraphenylbutane. Free-radical intermediates can account for the products (eq 4); however, a simple homolytic mechanism is  $\text{TS}^* + \text{Et}_3\text{N} \rightarrow \text{PhCH}_2\dot{\text{C}}\text{HPh} + \text{Et}_2\dot{\text{N}}\text{CHCH}_3 \rightarrow \text{PhCH}_2\text{CHPhCH}(\text{CH}_3)\text{NEt}_2 + \text{PhCH}_2\text{CH}_2\text{Ph} + (\text{PhCH}_2\text{CHPh})_2$  (4)

consistent with the observed solvent effect. For a constant amine concentration, quantum yields increase with increasing size of the alkyl group ( $\text{Me} < \text{Et} < i\text{-Pr}$ ). With secondary amines, addition of the N-H bond to stilbene occurs accompanied by the formation of 1,2-

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Table I  
Properties of *trans*-Stilbene Exciplexes

exciplex	$10^3 \nu_{\max}^a$ , $\text{cm}^{-1}$	$\mu$ , debye <sup>b</sup>	$\tau$ , ns <sup>c</sup>	$k_q \tau$ , $\text{m}^{-1}$ <sup>d</sup>	$\Delta G_{\text{ET}}$ , eV <sup>e</sup>
triethylamine	22.7	14.3	5	2.2	-0.4
<i>N,N</i> -diisopropylethylamine	23.0	15.6	16	3.9	-0.7
2,5-dimethyl-2,4-hexadiene	23.8	7.0	1	4.5	-0.1
dimethyl fumarate	19.2	12.3	2	5.4	-0.3
fumaronitrile	18.9	12.7	8	7.6	-0.5

<sup>a</sup> Frequency of the exciplex fluorescence maximum in nonpolar solvent. <sup>b</sup> Exciplex dipole moment calculated from eq 3. <sup>c</sup> Exciplex lifetime in nonpolar solvent. <sup>d</sup> Stern-Volmer fluorescence quenching constant in nonpolar solvent. <sup>e</sup> Free energy for electron transfer calculated from eq 2.

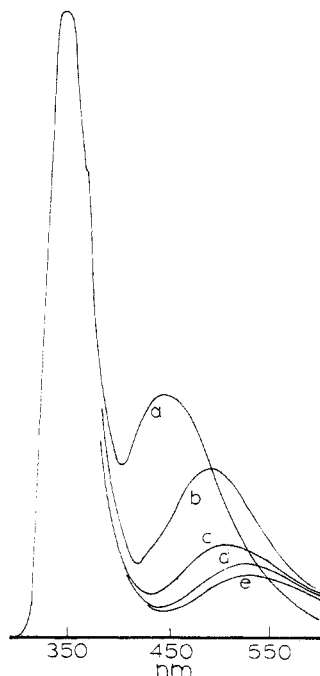
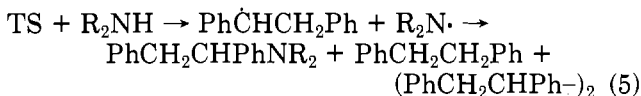


Figure 4. Corrected fluorescence spectra of *trans*-stilbene (350 nm) and the stilbene-triethylamine exciplex in (a) hexane, (b) 3:1 hexane/ethyl acetate, (c) 1:1 hexane/ethyl acetate, (d) 1:3 hexane/ethyl acetate, and (e) ethyl acetate.

diphenylethane and 1,2,3,4-tetraphenylbutane. These products implicate the presence of free-radical intermediates arising from N-H abstraction by singlet stilbene (eq 5). Unlike the case of tertiary amines,



product quantum yields for secondary amines decrease with increasing solvent polarity and increasing size of the alkyl group. Primary amines show chemical behavior similar to that of secondary amines, but are much less reactive.

The essential clue to the unraveling of the seemingly complex behavior of stilbene with alkylamines comes from the observation of exciplex fluorescence from stilbene-tertiary amines in nonpolar aprotic solvents. The fluorescence of the stilbene-triethylamine exciplex in mixed hexane-ethyl acetate solvent (Figure 4) illustrates the solvent dependence of frequency and intensity normally observed for aromatic hydrocarbon-tertiary amine exciplexes.<sup>3b,30</sup> Exciplex fluorescence frequency and lifetime in hexane, dipole moment (from eq 3 and the assumption of a 4.5-Å solvent cavity radius), fluorescence quenching constant (see also Figure 5) and calculated free energy for full

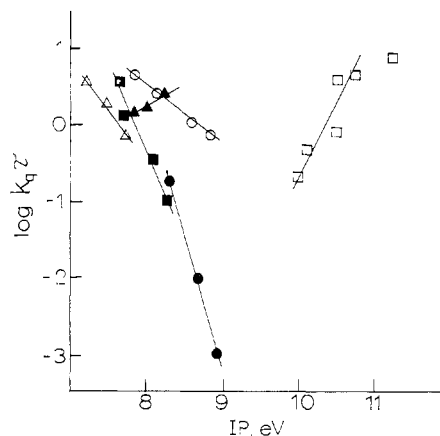
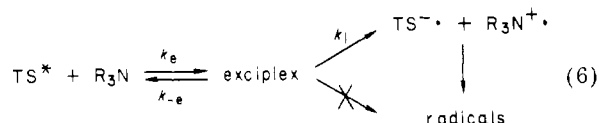


Figure 5. *trans*-Stilbene fluorescence quenching constants for ( $\Delta$ ) tertiary amines, ( $\blacktriangle$ ) secondary amines, ( $\bullet$ ) alkenes, ( $\circ$ ) dienes, ( $\blacksquare$ ) vinyl ethers, and ( $\square$ ) electron-poor alkenes vs. quencher ionization potential.

electron transfer are given in Table I for stilbene-triethylamine and -diisopropylethylamine exciplexes. As expected, the better electron donor forms a more polar, longer lived exciplex. In Figure 3b relative exciplex fluorescence yields and amine addition yields are plotted as a function of solvent dielectric constant. The form of this Figure 3b is strikingly similar to that of Figure 3a, from which we infer that electron transfer to form a pair of radical ions ( $k_i$ ) must occur prior to free-radical formation (eq 6). Full electron transfer is



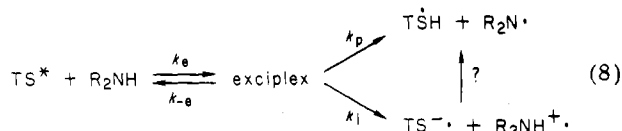
apparently necessary to render the  $\alpha$ -C-H bond sufficiently acidic for proton transfer to occur. In support of proton transfer from an amine cation radical, we have recently observed that the exclusive addition product from singlet stilbene and diisopropylmethylamine arises from cleavage of the methyl  $\alpha$ -C-H bond (eq 7).<sup>16b</sup>



This result is compatible with proton transfer from an amine cation radical, but not with a free-radical abstraction mechanism.

No exciplex fluorescence has been observed for stilbene-secondary amine solutions; however, evidence for reversible exciplex formation is provided by the negative temperature dependence of the fluorescence quenching rate constant.<sup>31</sup> The absence of exciplex fluorescence from aromatic hydrocarbon-secondary

amine exciplexes is known to result from very rapid hydrogen transfer (eq 8,  $k_p > 10^{10} \text{ s}^{-1}$ ).<sup>32</sup> In polar

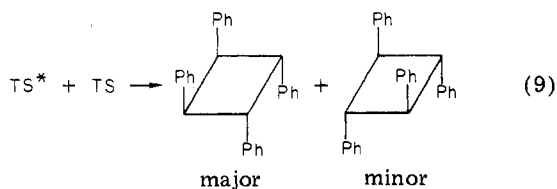


solvents radical ion formation competes with hydrogen transfer,<sup>29</sup> which may account for the decrease in yield of addition products with increasing solvent polarity. The unusual decrease in reactivity with decreasing secondary amine ionization potential (Figure 5) is consistent with the mechanism shown in eq 8. Electron-releasing alkyl groups should stabilize the electron-deficient amine nitrogen in the exciplex, thus diminishing its acidity and the rate of hydrogen transfer ( $k_p$ ). Apparently this effect is large enough to counteract the increase in  $k_e/k_{-e}$  with decreasing amine ionization potential.

As we have seen, exciplex formation is the sine qua non for reaction of stilbene with alkylamines. The remarkably different behavior of tertiary vs. secondary amines is a consequence of the chemical behavior of the exciplexes. Stilbene-tertiary amine exciplexes have no chemically productive decay pathways in nonpolar solvents, thus allowing exciplex fluorescence to compete with nonradiative decay. In polar solvents, radical ion formation provides a chemically productive decay channel. In contrast, stilbene-secondary amine exciplexes have a very efficient decay pathway (eq 8) which precludes the observation of exciplex fluorescence even in nonpolar solvents. It is interesting to note that tertiary and secondary amines display similar fluorescence quenching rate constants (Figure 5) even though tertiary amines are better electron donors. The greater stability ( $k_e/k_{-e}$ ) of the tertiary amine exciplexes is offset by the greater chemical reactivity ( $k_p$ ) of the secondary amine exciplexes. The low reactivity of stilbene with primary alkylamines is simply a consequence of their high ionization potentials, which results in little or no charge-transfer stabilization of the exciplex. The gross mechanistic features of stilbene-amine exciplex chemistry are similar to those reported for aromatic hydrocarbon-amine reactions,<sup>33</sup> and it is likely that exciplex intermediates play a similar part in these reactions.

### Dimerization and Cycloaddition with Electron-Rich Alkenes and Dienes

The photodimerization of stilbene was observed by Ciamician and Silber<sup>34</sup> in 1902 and subsequently found to produce more cis,trans,cis than all-trans dimer (eq 9).<sup>35</sup> Self-quenching of stilbene fluorescence and trans



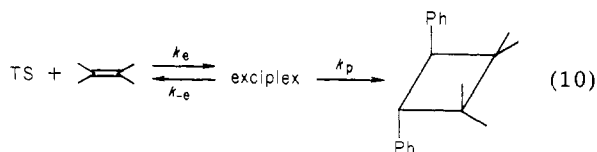
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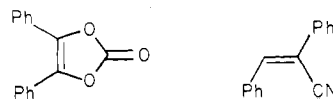
→ cis isomerization occur near the diffusion-controlled limit in benzene solution.<sup>36</sup> Excimer fluorescence is not observed at room temperature but has been reported for  $\gamma$  irradiation of stilbene in a squalene glass at 77 K.<sup>37</sup> Since the quantum yield<sup>38</sup> for dimerization is high ( $\Phi \sim 0.5$ ), rapid dimerization may account for the absence of excimer fluorescence, as is the case for the anthracene excimer.<sup>39</sup>

The efficient ( $\Phi = 1.0$ ) photochemical addition of stilbene to tetramethylethylene (eq 10) was reported by



Chapman in 1968.<sup>40</sup> Subsequent observation of an inverse temperature dependence for the cycloaddition rate constant provided evidence for an exciplex intermediate.<sup>41</sup> It was further established that stilbene cycloaddition occurred exclusively from the trans singlet state with complete retention of stilbene and alkene stereochemistry.<sup>42</sup> Concurrent reports of nonstereospecific addition of stilbene and cyclic vinyl ethers<sup>43a,b</sup> have recently been found to be erroneous.<sup>43c</sup> Complete retention of stilbene and alkene stereochemistry has been observed in addition reactions with acyclic vinyl ethers,<sup>18b</sup> dienes,<sup>19</sup> and  $\alpha,\beta$ -unsaturated esters.<sup>17</sup>

*trans*-Stilbene also reacts efficiently ( $\Phi = 0.5-1.0$ ) with conjugated dienes to yield [2 + 2] cycloadducts.<sup>19</sup> Weak exciplex emission has been observed from *trans*-stilbene-2,5-dimethyl-2,4-hexadiene.<sup>19b</sup> From the solvent dependence of exciplex fluorescence the dipole moment of this exciplex is estimated to be 7 D, much lower than the values for stilbene-amine exciplexes. Since electron transfer from the diene to singlet stilbene is calculated to be only slightly exothermic (Table I), it is not surprising that the exciplex is relatively nonpolar. No exciplex emission is observed for stilbene with dienes of higher ionization potential or for any of the alkenes or vinyl ethers examined (Figure 5). However, exciplex fluorescence is observed for the electron-deficient stilbene derivatives diphenylvinylene carbonate and  $\alpha$ -cyanostilbene with conjugated di-



enes.<sup>19c</sup> Exciplex fluorescence is thus observed only

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(38) All quantum yields are limiting values obtained from plots of  $\Phi^{-1}$  vs. [quencher]<sup>-1</sup>.

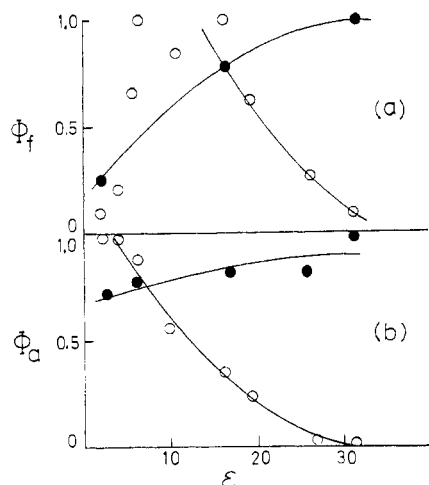
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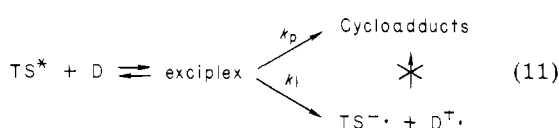
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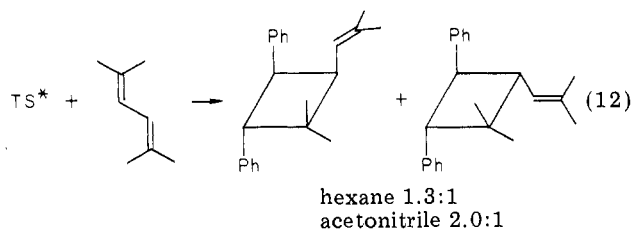
**Figure 6.** (a) Relative exciplex fluorescence intensity and (b) relative cycloaddition quantum yields for *trans*-stilbene- (●) and diphenylvinylene carbonate-2,5-dimethyl-2,4-hexadiene exciplexes (○) vs. solvent dielectric constant.

when  $\Delta G_{ET}$  (eq 2) is calculated to be exothermic.

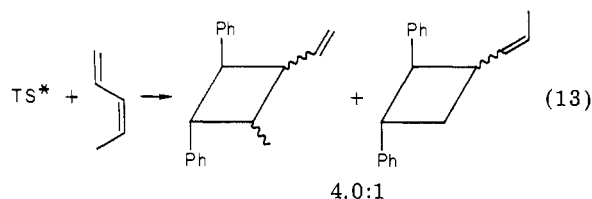
The solvent dependence of the stilbene–diene exciplex fluorescence intensity is shown in Figure 6a along with that for the more polar diphenylvinylene carbonate–diene exciplex ( $\mu \sim 10$  D). It is interesting to note that more polar solvents are necessary to effect a decrease in the diphenylvinylene carbonate–diene exciplex fluorescence intensity than is the case for the more polar stilbene–amine (Figure 3b). Moreover, the relatively nonpolar stilbene–diene exciplex shows no decrease in intensity over the range of solvent polarity investigated. The quantum yields for cycloadduct formation from the stilbene- and diphenylvinylene carbonate–diene exciplexes show a solvent dependence (Figure 6b) similar to that for exciplex fluorescence. From this and other evidence we conclude that cycloaddition occurs exclusively from the exciplex and not from the radical ion pair formed in polar solvents (eq 11).



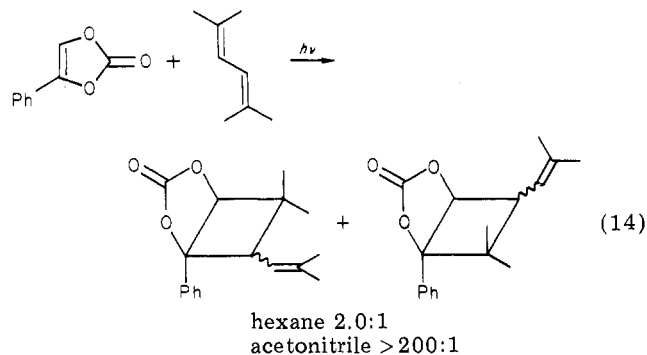
The reactions of singlet stilbene with dienes provide a wealth of stereochemical information about the cycloaddition process. As is the case for stilbene dimerization (eq 9), a slight preference is observed for formation of the thermodynamically less stable isomer (eq 12), a preference which is enhanced in more polar



solvents.<sup>19a</sup> This preference finds analogy in the Alder endo rule for thermal [4 + 2] cycloaddition and may be indicative of a role for secondary  $\pi$ -orbital stabilization of the exciplex.<sup>44</sup> Cycloaddition of stilbene with nonsymmetric dienes occurs preferentially at the more substituted double bond (eq 13).<sup>19b</sup> This unusual



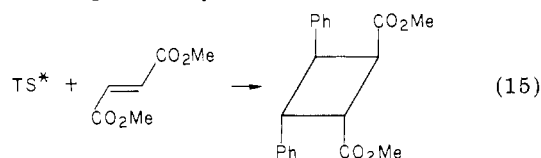
regioselectivity is analogous to periselectivity in thermal [4 + 2] cycloaddition reactions and can be attributed to higher frontier molecular orbital coefficients at the more substituted double bond (vide infra).<sup>44</sup> An interesting example of solvent-enhanced regioselectivity was encountered in the reaction of singlet phenylvinylene carbonate with dienes (eq 14).<sup>45</sup> One im-



portant difference between singlet stilbene [2 + 2] cycloaddition reactions and thermal cycloaddition is the apparent insensitivity of the former reactions to steric effects. The quantum yields of alkene, vinyl ether, and diene cycloaddition all increase with increasing alkylation. Alkylation increases exciplex stability ( $k_e/k_e^-$ ), and thus a small steric effect on exciplex cycloaddition ( $k_p$ ) might serve only to attenuate the dependence of reactivity ( $k_q$ ) on donor ionization potential (Figure 5).

### Electron-Poor Alkenes

Singlet *trans*-stilbene undergoes [2 + 2] cycloaddition reactions with a number of electron-poor alkenes ( $\alpha$ , $\beta$ -unsaturated esters and nitriles).<sup>17</sup> Fluorescence quenching rate constants (Figure 5) increase with increasing alkene electron affinity, indicating that *trans*-stilbene acts as the electron donor in these reactions. The cycloaddition reactions of singlet stilbene with electron-poor alkenes are, in general, much less efficient than the reactions with electron-rich alkenes and dienes. For example, the addition of singlet stilbene and dimethyl fumarate yields dimethyl  $\mu$ -truxinate (eq 15) with a quantum yield of 0.04.<sup>17,38</sup>



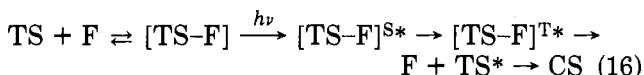
Stilbene–dimethyl fumarate exciplex fluorescence (Table I) and cycloaddition yields decrease with increasing solvent polarity, and neither process can be detected in solvents more polar than tetrahydrofuran. Cycloaddition thus occurs from the exciplex but not from the radical ion pair (eq 11). Since stilbene and dimethyl fumarate form a weak ground-state complex,

(44) I. Fleming, "Frontier Orbitals and Organic Chemical Reactions", Wiley-Interscience, London, 1976, Chapter 4.

(45) F. D. Lewis and D. E. Johnson, *Mol. Photochem.*, 8, 425 (1977).

it is possible to compare the behavior of uncomplexed and complexed stilbene using excitation at 334 and 365 nm, respectively. Similar cycloaddition quantum yields and exciplex fluorescence are observed. Thus the same excited-state complex must be formed in both processes, either directly or by rapid relaxation of the initially formed excited state.

Addition of singlet stilbene to fumaronitrile does not occur even though a strongly fluorescent, long-lived exciplex (Table I) is formed. Again, the same exciplex lifetime and spectral distribution are obtained upon excitation of the weak ground-state complex at 390 nm and excitation of stilbene at 330 nm. Excitation of the charge-transfer complex also results in formation of *cis*-stilbene. Since exciplex formation is irreversible and *cis*-stilbene formation is significantly increased in the presence of oxygen,<sup>17c</sup> we suggest that *cis*-stilbene formation results from intersystem crossing (oxygen enhanced<sup>46</sup>) of the singlet exciplex to a triplet exciplex. The triplet exciplex then dissociates to fumaronitrile (F) and triplet stilbene,<sup>47</sup> which is known to decay with near equal probability to *cis*- and *trans*-stilbene (eq 16).<sup>20</sup>

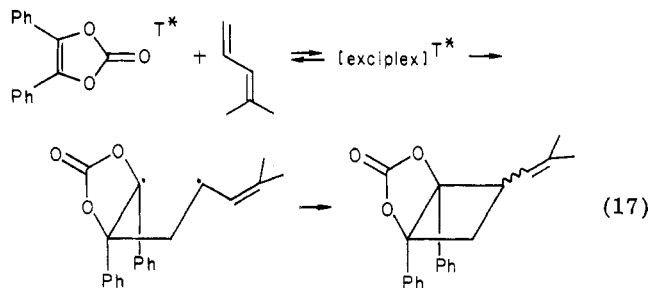


No cycloadducts have been observed upon irradiation of stilbene with the strong electron acceptors maleic anhydride and tetracyanoethylene. Irradiation of *trans*-stilbene and maleic anhydride in nonpolar solvents results in formation of the dimers of both reactants,<sup>17b</sup> but no crossed adduct. Irradiation in polar solvents results in formation of an alternating copolymer, presumably via a radical ion mechanism.<sup>48</sup>

### Triplet-State Reactions

Efforts to detect reactions of triplet stilbene with alkenes and dienes have been unsuccessful. Since triplet exciplexes are in general less stable than their singlet counterparts,<sup>3</sup> it is possible that triplet *trans*-stilbene simply does not form stable exciplexes with alkenes and dienes. This explanation is consistent with the observation of stilbene isomerization from the stilbene-fumaronitrile exciplex (eq 16). It is also possible that twisting about the central double bond of triplet stilbene is too rapid to allow formation of an exciplex with the usual sandwich-type geometry.

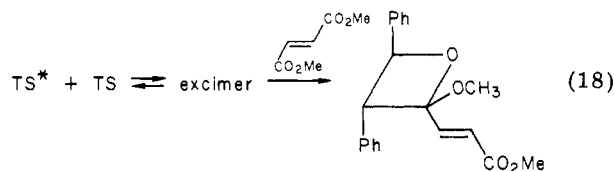
Triplet-state cycloaddition reactions have been obtained from diphenylvinylene carbonate with alkenes and dienes.<sup>49</sup> These reactions are nonstereospecific, as expected for product formation via a biradical intermediate (eq 17). While there is currently no spectroscopic evidence for a triplet exciplex precursor of the biradical intermediate, chemical evidence supports such a mechanism. The regioselectivity of the diene adducts is similar to that for thermal [2 + 2] addition to dienes; however, stereochemical labeling



studies have shown that the regioselectivity of initial bonding is the same as that observed in the singlet reactions.<sup>49b</sup> Moreover, the solvent dependence of addition of triplet diphenylvinylene carbonate to vinyl ethers<sup>49c</sup> and dienes<sup>49b</sup> is similar to that for the singlet reaction (Figure 6b). One important difference between singlet and triplet cycloaddition is the operation of steric effects in the latter reactions. Triplet cycloaddition does not occur at tri- and tetrasubstituted double bonds. Our investigation of diene addition reactions indicated that the steric effect operates on biradical cyclization versus collapse ( $k_p/k_c$ ), the more substituted biradical cyclizing less efficiently.<sup>49b</sup>

### Termolecular Reactions

During the course of our investigation of the stilbene-dimethyl fumarate system, we observed that at high stilbene concentrations an oxetane adduct is formed at the expense of dimethyl  $\beta$ -truxinate which is the predominant product at low stilbene concentration (eq 15).<sup>17</sup> Investigation of the oxetane-forming reaction showed that it resulted from reaction of stilbene excimer with dimethyl fumarate (eq 18). Excimer



and exciplex quenching by a third molecule is a well-documented process<sup>50</sup> which, in some cases, results in formation of bimolecular addition products.<sup>14,51</sup> However there are no previous examples of the formation of different cycloadducts from a singlet monomer and excimer. The chemistry of excited-state termolecular complexes presents an exciting new frontier for exploratory photochemistry.

### Concluding Remarks

The common denominator for all stilbene photochemical addition reactions is the intermediacy of an exciplex or excimer. The overall reaction can therefore be analyzed in two steps: exciplex formation and covalent bond formation. Perturbation theory should be applicable to the formation of weakly bound exciplexes. Indeed, frontier molecular orbital (FMO) theory has enjoyed some of its greatest successes in applications to bimolecular photochemical reactions.<sup>52,53</sup> Exciplex

(46) (a) H. Hayashi and S. Nagakura, *Chem. Phys. Lett.*, **53**, 201 (1978); (b) R. A. Caldwell, *J. Phys. Chem.*, **82**, 2644 (1978).

(47) For examples of the formation of aromatic hydrocarbon triplets from singlet exciplexes see: T. Nishimura, N. Nakashima, and N. Mataga, *Chem. Phys. Lett.*, **46**, 344 (1977).

(48) M. L. Hallensleben, *Eur. Polym. J.*, **9**, 227 (1973).

(49) (a) F. D. Lewis and R. H. Hirsch, *Tetrahedron Lett.*, 2651 (1975); (b) F. D. Lewis and R. H. Hirsch, *J. Am. Chem. Soc.*, **98**, 5914 (1976); (c) F. D. Lewis, R. H. Hirsch, P. M. Roach, and D. E. Johnson, *ibid.*, **98**, 8438 (1976).

(50) D. Creed, R. A. Caldwell, H. Ohta, and D. C. DeMarco, *J. Am. Chem. Soc.*, **99**, 277 (1977).

(51) R. O. Campbell and R. S. H. Liu, *Mol. Photochem.*, **6**, 207 (1974).

(52) Reference 44, Chapter 6.

(53) (a) W. C. Herndon, *Chem. Rev.*, **72**, 157 (1972); (b) N. D. Epitios, *J. Am. Chem. Soc.*, **94**, 1924, 1935, 1941 (1972); (c) K. N. Houk, *Acc. Chem. Res.*, **8**, 361 (1975).

stabilization is the result of Coulombic attraction and FMO interactions (eq 19, where  $Q$  is the charge on the

$$\Delta E = \sum \frac{Q_D Q_A}{\epsilon R_{DA}} + \sum \frac{(H_{DA})^2}{E_D - E_A} \quad (19)$$

atoms of the donor and acceptor molecules,  $R_{DA}$  is the distance between these atoms,  $H_{DA}$  is the effective frontier orbital overlap, and  $E_D - E_A$  is the energy difference between interacting frontier orbitals). The most stable stilbene exciplexes are formed when the Coulombic term is large ( $\Delta G_{ET}$  exothermic, eq 2), and it is only for such exciplexes that exciplex fluorescence has been observed. Orbital overlap ( $H_{DA}$ ) appears to influence cycloaddition stereochemistry (eq 9, 13–16) and reactivity (Figure 5). For donor quenchers of comparable ionization potential ( $E_D - E_A$  constant), fluorescence quenching rate constants increase in the order of increasing orbital overlap (alkenes < vinyl ethers < dienes). Similarly, for acceptor quenchers of comparable reduction potential, unsaturated esters are more reactive than chloroethylenes. Finally, for a series of related quenchers (e.g., dienes) orbital overlap is nearly constant and reactivity increases with decreasing values of  $E_D - E_A$  (Figure 5). It should be noted that when  $\Delta G_{ET}$  is highly exothermic,  $E_D - E_A$  is large and low yields of cycloaddition products are obtained from stilbene exciplexes.

Simple perturbation theory appears to be applicable to exciplex formation; however, exciplex bond formation is an altogether different matter. The familiar energy surfaces for [2 + 2] cycloaddition which derive from the state correlation diagram of Longuet-Higgins are shown in Figure 1c.<sup>54</sup> The diexcited configurations of the donor and acceptor ( $D^*$ ,  $A^*$ ) descend to define the potential well of the product. The pseudocrossing of the diexcited- and ground-state surfaces produces a barrier for thermal cycloaddition and a pericyclic

minimum or funnel in the excited-state surface. According to Michl,<sup>55</sup> exciplex cycloaddition requires a real crossing of the exciplex and the excited-state surface which defines the pericyclic minimum.<sup>56</sup> This crossing (Figure 1d) can lead to an energy barrier which will determine the rate constant for cycloaddition. Caldwell<sup>57</sup> has recently determined the activation parameters for cycloaddition of several exciplexes and finds values ( $\Delta H^\ddagger = 2\text{--}5$  kcal/mol,  $\Delta S^\ddagger = -(11\text{--}16)$  eu) which are consistent with a small thermal barrier and moderate bond reorganization. Furthermore, the barrier increases as the extent of exciplex charge-transfer stabilization increases, in agreement with our observation that nonpolar stilbene exciplexes form cycloadducts more efficiently than polar exciplexes. We have also found that the rate constant for the diphenylvinylene carbonate–2,5-dimethyl-2,4-hexadiene exciplex cycloaddition decreases with increasing solvent polarity.<sup>19c</sup> Apparently, both solvation and substitution serve to stabilize the polar exciplex more than the transition state leading to the pericyclic minimum. While the energy surfaces in Figure 1d accommodate many features of the singlet exciplex cycloaddition process, several fundamental aspects of exciplex chemistry remain to be elucidated. Among these are (a) the nature of the nonradiative decay processes that compete with cycloaddition, (b) the factors (steric, electronic, etc.) that govern cycloaddition reactivity, and (c) the nature of the reaction pathways for ionic and triplet-state cycloaddition reactions.

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(54) (a) H. C. Longuet-Higgins and E. W. Abrahamson, *J. Am. Chem. Soc.*, **87**, 2045 (1965); (b) W. T. A. M. van der Lugt and L. J. Oosterhoff, *ibid.*, **91**, 6042 (1969).

(55) J. Michl, *Photochem. Photobiol.*, **25**, 141 (1977).

(56) See also: N. D. Epiotis and S. Shaik, *J. Am. Chem. Soc.*, **100**, 9 (1978).

(57) R. A. Caldwell and D. Creed, *J. Chem. Soc.*, **100**, 2905 (1978).