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Divergent Cycloaddition Pathways for Reaction of Singlet Stilbene and Stilbene Excimer with Dimethyl Fumarate

Sir:

The intermediacy of excimers and exciplexes in photochemical cycloaddition reactions is firmly established.[1] Furthermore, excimers and exciplexes often have sufficiently long lifetimes to be intercepted by a third molecule.[2-6] Such interception can result in the formation of a triplex,[2] exciplex substitution to form a new exciplex,[3] deactivation to ground-state molecules,[4,5] or new or enhanced chemical reactions.[6] We wish to report that different cycloadducts are formed upon quenching of singlet trans-stilbene and stilbene excimer by dimethyl fumarate. Divergent modes of cycloaddition for a singlet monomer and excimer are without precedent and offer a promising avenue for extending the synthetic scope of the photochemical cycloaddition process.

Preparative photolysis of trans-stilbene (7×10^{-3} M) and dimethyl fumarate (7×10^{-2} M) in benzene has previously been reported to yield dimethyl μ- and neo-truxinate (**1** and **2**) as the major and minor isolated products.[7] Photolysis of a more concentrated solution of stilbene (0.20 M) and dimethyl fumarate (0.22 M) followed by silica gel chromatography led

Table I. Quantum Yields for Stilbene Isomerization and Cycloaddition[a]

[trans-Stilbene], M	[Dimethyl fumarate], M	Φ_t	Φ_1	Φ_3
0.010	0.13	0.31	0.0080	0.0010
0.010	0.17	0.28	0.0094	0.0012
0.010	0.25	0.25	0.014	0.0014
0.010	0.39	0.20	0.017	0.0013
0.10	0.13	0.33	0.0081	0.036
0.10	0.17	0.29	0.0096	0.037
0.10	0.25	0.24	0.012	0.036
0.10	0.33	0.21	0.015	0.036
0.010	0.10	0.35	0.0069	0.0017
0.050	0.10	0.39	0.0070	0.013
0.10	0.10	0.38	0.0069	0.036
0.25	0.10	0.25	0.0061	0.16
0.55	0.10	0.20	0.0051	0.24

[a] Degassed 1% pyridine/benzene solutions irradiated using monochromatic 334-nm light at 25 °C. Analysis by gas chromatography at <5% conversion on a 5 ft × 1/8 in. 5% SF96 on Chromosorb G column at 220 °C. Light intensities determined by benzophenone–benzyhydrol actinometry. Limits of error: ±10% for stilbene isomerization, ±20% for cycloadduct formation.

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

λ, nm[c]	Φ_t	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 note for Table I. [c] Wavelength of irradiation.

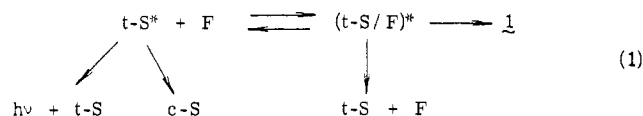$$\underset{1}{\qquad} \quad \underset{2}{\qquad} \quad \underset{3, 4}{\qquad}$$
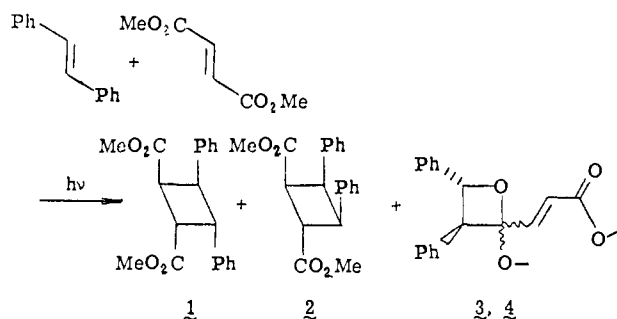
to isolation of **1** and **2** along with two previously unreported isomeric oxetanes (**3** and **4**).[8,9] At low trans-stilbene conversions, cis-stilbene, **1**, and **3** were the only products detected by GC. As the stilbene photostationary state was approached, **2** and **4** were detected. Michler's ketone and benzil sensitized the isomerization of trans-stilbene (0.01 M) in the presence of dimethyl fumarate (0.10 M); however, no cycloadducts were observed at moderate to high conversions of trans- to cis-stilbene.

Quantum yields for trans-stilbene isomerization (Φ_t) and formation of **1** and **3** were determined as a function of both dimethyl fumarate and trans-stilbene concentration (Table I). Stilbene and dimethyl fumarate form a weak ground-state complex ($K \sim 1.0 \pm 0.5$ by the method of Rose and Drago[10]); however, for all of the data in Table I, essentially all ($\geq 98\%$) of the 334-nm light is absorbed by uncomplexed trans-stilbene. Selective excitation of the ground-state complex can be accomplished by irradiation of concentrated solutions at 365 nm and results in different product quantum yields than those obtained with 334-nm irradiation (Table II). The fluorescence of dilute (10^{-4} M) trans-stilbene is efficiently quenched by dimethyl fumarate with the concomitant appearance of weak exciplex fluorescence (λ_{max} 470 nm, benzene solution).

The failure of triplet sensitization to effect either cyclobu-

tane or oxetane formation establishes that singlet stilbene is a precursor of both cycloadducts, as is the case for stilbene additions to electron-rich alkenes.[11] At low stilbene concentration (0.01 M) cyclobutane **1** is the major product and a plot of $\Phi_1{}^{-1}$ vs. [fumarate]$^{-1}$ is linear, as expected for a singlet cycloaddition process. The observation of weak exciplex fluorescence and the stereospecific formation of the dimethyl truxinate with maximum π-orbital overlap[7] are both consistent with an exciplex intermediate (eq 1). The low limiting quantum

$$\begin{array}{ccc}
\text{t-S}^* + \text{F} & \xrightleftharpoons & (\text{t-S}/\text{F})^* \longrightarrow \underline{1} \\
\end{array} \tag{1}$$

hν + t-S   c-S   t-S + F

yield for cyclobutane formation (0.04) indicates the presence of other efficient exciplex decay channels, as is the case for the phenanthrene–dimethyl fumarate exciplex.[12] Interestingly, the limiting quantum yield is similar to the quantum yield for formation of **1** upon excitation of the stilbene–dimethyl fumarate ground-state complex (Table II).[13]

Quantum yields for oxetane formation (Φ_3) increase with increasing stilbene concentration, but are relatively insensitive to dimethyl fumarate concentration (Table I). Oxetane formation via interception of stilbene excimer by ground-state dimethyl fumarate (eq 2) provides the only satisfactory ex-

$$\text{t-S}^* + \text{t-S} \xrightleftharpoons (\text{t-S})_2{}^* \xrightarrow{\text{F}} \underline{3} \tag{2}$$

Dimer
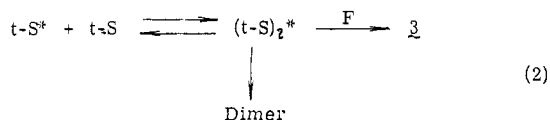
planation of the stilbene dependence of Φ_3.[14] Self-quenching of stilbene fluorescence and isomerization become significant for stilbene concentrations above 10^{-2} M.[15] Stilbene excimer fluorescence has been observed following γ irradiation of stilbene in a squalene glass at 77 K,[16] but cannot be detected at room temperature in solution, presumably owing to the efficient formation of stilbene dimer.[15] Increasing dimethyl fumarate concentration would be expected to increase Φ_3 according to eq 2; however, quenching of stilbene singlet by dimethyl fumarate (eq 1) inhibits stilbene excimer formation. The concurrent operation of eq 1 and 2 leads to complex kinetics which will be discussed in a full paper.

In conclusion, quenching of singlet *trans*-stilbene by dimethyl fumarate results in formation of cyclobutane **1**, whereas quenching of stilbene excimer results in formation of oxetane **3**. We are currently investigating other cases in which the bimolecular chemistry of the singlet state differs from that of the excimer or exciplex.[17]

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115. The minor oxetane **4** could not be isolated in pure form; however its NMR spectrum was similar to that of **3**.
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Determination of Critical Micelle Concentrations in Micellar and Reversed Micellar Systems by Positron Annihilation Techniques[1]

Sir:

An important parameter in the study of micellar systems,[2] whose relevance in energy conversion and storage as well as in tertiary oil recovery is well recognized, is the so-called critical micelle concentration (cmc). The critical micelle concentration is defined as the narrow range of surfactant concentration at which the micelles first become detectable, usually by some change in the physical properties, such as interfacial tension, electric conductivity, emf, pH, specific heat, viscosity and the optical and spectroscopic properties of the solution. These methods generally provide clear evidence for the formation of micelles; however, since the observed variation of the above physical properties at the cmc is not abrupt but occurs more or less gradually, extrapolations are required which in turn introduce an uncertainty in the determination of the cmc.

In the following we would like to discuss the applicability of the positron annihilation technique[3] as a simple method for the accurate determination of cmc. This method takes advantage of the fact that the lifetime and the annihilation characteristics of a positron and the formation of the positronium atom (Ps), which is the bound state of a positron and an electron, are determined by their microscopic chemical and physical environment.[3]

The sensitivity of, e.g., the positronium formation process toward structural changes has already been previously recognized in experiments with liquid crystals,[4-7] where the variations in the mesomorphic phases were clearly reflected in the positron lifetime characteristics. Thus one could expect that the formation of micelles leading to structural changes in the solution should also result in distinct variations of the positron lifetime parameters.

In the following, we should like to report the results of a preliminary study of positron interactions in solutions with various amounts of surfactants present. Six different micellar systems were studied. Dodecylammonium propionate (DAP) in benzene, cyclohexane, and *n*-hexane; sodium di(2-ethylhexyl)sulfosuccinate (Aerosol OT or AOT) in benzene; sodium decylsulfate (NaDS) and decyltrimethylammonium bromide (DTAB) in water.