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Photodimerization of Singlet *trans*- and *cis*-Anethole. Concerted or Stepwise?

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Abstract: The singlet states of both *trans*- and *cis*-anethole are moderately long-lived (8.5 and 6.1 ns, respectively) and undergo photodimerization as well as cis,trans isomerization. Both the singlet lifetimes and fluorescence rate constants are larger than those for related phenylalkenes. Dimerization of singlet *trans*-anethole yields exclusively a syn head-to-head dimer with a rate constant of 3.2×10^8 M^{-1} s^{-1}. Reaction of singlet *trans*-anethole with ground-state *cis*-anethole also yields a syn head-to-head dimer with a lower rate constant. Dimerization of singlet *cis*-anethole yields an anti head-to-head dimer with a rate constant of 0.8×10^8 M^{-1} s^{-1}. Whereas the two former reactions occur with retention of anethole stereochemistry, dimerization of *cis*-anethole occurs with retention at one double bond and inversion at the other. Dimerization of *cis*-anethole is proposed to occur via sequential formation of a singlet exciplex with optimized π-orbital overlap and a singlet 1,4-biradical intermediate.

Introduction

The $[2_s + 2_s]$ cycloaddition reaction of a singlet olefin and ground-state olefin is a prototypical symmetry-allowed process.[1] There are numerous examples of stereospecific [2 + 2] photocycloaddition reactions, in accord with the simplest interpretation of covalent bond formation as a concerted process.[2] For example, cycloaddition of singlet *trans*-stilbene with *cis*- or *trans*-2-butene[3] and with dimethyl maleate or fumarate[4] occurs with complete retention of olefin stereochemistry. A more stringent test of photocycloaddition stereospecificity would be posed by the reaction of singlet and ground-state cis olefins. With the exception of the photodimerization of *cis*-2-butene,[2b] attempts to observe such processes have been frustrated by competing cis → trans photoisomerization and by the lower inherent reactivity of cis vs trans olefins as the singlet or ground-state component in photocycloaddition reactions.[4,5] We report here the results of our investigation of the [2 + 2] photodimerization reactions of singlet *trans*-anethole (1-(*p*-methoxyphenyl)propene, t-A) and *cis*-anethole (c-A). Whereas the reaction of singlet t-A with either ground-state t-A or c-A occurs with retention of stereochemistry, the dimerization of c-A occurs with complete inversion of stereochemistry at one of the two double bonds.

Results and Discussion

Photophysics and Photoisomerization. Absorption and fluorescence data for t-A and c-A in hexane solution are reported in Table I. The absorption spectra of the trans and cis isomers exhibit maxima at 258 and 254 nm and less intense long-wavelength shoulders at 300 and 290 nm (estimated from first derivative spectra). By analogy with the absorption spectra of the 1-phenylpropenes, the maxima are assigned to an allowed HOMO → LUMO transition to a delocalized $^1A_1$ state and the shoulders to a forbidden benzene-localized transition to a $^1B_2$ state.[6] The higher energy and intensity of the A band for the cis vs trans isomer is attributed to nonplanarity of the cis isomer which results from nonbonded repulsion of the methyl and aryl groups.[7]

Both t-A and c-A exhibit structureless fluorescence with maxima at 326 and 318 nm, respectively. Long-wavelength maxima in the fluorescence excitation spectra occur at 297 nm for t-A and 288 nm for c-A. Fluorescence is presumed to originate from the low-energy $^1B_2$ state, as is the case for the 1-phenylpropenes.[6] Fluorescence lifetimes and quantum yields (Table II) were obtained with dilute solutions (10^{-4} M) in order to avoid self-absorption of fluorescence, which might result from overlapping absorption and emission spectra and shortening of the singlet lifetime resulting from self-quenching.[8]

Table I. Absorption and Fluorescence Spectral Data for the Anetholes

	absorption		fluorescence[a]	
isomer	λ_{max}	ϵ	λ_{ex}	λ_f
trans	258	19750	297	326
	300 (sh)	1780		
cis	254	18380	288	318
	290 (sh)	1390		

[a] Data for 10^{-4} M hexane solution.

Table II. Kinetics and Isomerization Quantum Yields for Singlet and Triplet Anetholes[a]

isomer	τ_s, ns	Φ_f	$10^{-7}k_f$	$\Phi_i(S)^b$	$\Phi_i(T)^c$
trans	8.5 ± 0.1	0.57 ± 0.03	6.7	0.12 ± 0.01	0.23
cis	6.1 ± 0.1	0.30 ± 0.02	4.9	0.06 ± 0.01	0.16

[a] Fluorescence data for 10^{-4} M deoxygenated hexane solutions. [b] Quantum yield extrapolated to zero concentration for direct irradiation (313 nm) in deoxygenated acetonitrile solution. [c] Values for triplet-sensitized irradiation (365 nm) of the anetholes (0.05 M) with Michler's ketone (3×10^{-3} M) in degassed acetonitrile solution.

Table III. Quantum Yields for Photoisomerization of the Anetholes[a]

	Φ_i	
concn, M	trans	cis
0.02	0.119 ± 0.005	0.06 ± 0.01
0.03		0.06
0.04	0.112	0.06
0.06	0.104	0.06
0.08	0.102	0.06
0.10	0.100	0.07

[a] Data for 313-nm irradiation of deoxygenated acetonitrile solutions.

The singlet lifetimes of the anetholes are longer than that of *trans*-1-phenylbutene (4.3 ns).[9] Both the singlet lifetime and fluorescence quantum yield are larger for t-A vs c-A. However, the fluorescence rate constants, calculated from the measured singlet lifetimes and fluorescence yields ($k_f = \Phi_f\tau_s^{-1}$), are similar for the two isomers. The similarity of k_f for the trans and cis isomers is consistent with the occurrence of fluorescence from a

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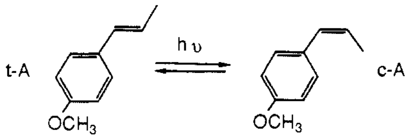
benzene-localized $^1B_2$ state.[6] The values of k_f (ca. 5 × 10^7 s^{-1}) are somewhat larger than the value for styrene (1.6 × 10^7 s^{-1}) and other phenylalkenes.[9,10] A similar increase in k_f is observed for anisole vs benzene (3.5 × 10^7 s^{-1} vs 2.4 × 10^6 s^{-1}) and is attributed to the interaction of the unpaired electrons on oxygen with the benzene π electrons.[11]

Since the k_f values for t-A and c-A are similar, the shorter lifetime of the cis isomer must result from more rapid nonradiative decay. Nonradiative decay of singlet styrene derivatives can occur via twisting of the double bond, internal conversion, and intersystem crossing.[9] Quantum yields for isomerization (Φ_i) of t-A and c-A, eq 1, were measured for 0.02–0.10 M acetonitrile solutions with 313-nm irradiation (Table III). The measured value of Φ_i for t-A decreases with increasing concentration. A value of Φ_i = 0,12 ± 0.01 is obtained by extrapolating the low-concentration data to zero concentration. The concentration dependence of Φ_i, like the previously reported concentration dependence of τ_s for styrene, is presumably a consequence of excimer formation (vide infra).[8] Values of Φ_i for c-A proved more difficult to measure due to the stronger absorption of the trans vs cis isomer (ϵ_{313} = 310 vs 30) and its larger isomerization quantum yield. Correction of the measured values for light absorption by t-A provides values of Φ_i = 0.06 ± 0.01 which are not noticeably dependent upon concentration. The photostationary state obtained upon irradiation of 10^{-3} M t-A or c-A is 92 ± 2% c-A, in reasonable agreement with the value of 95% calculated from the measured quantum yields and absorbance at 313 nm. Dimerization does not compete effectively with isomerization in 10^{-3} M solutions. The lower quantum yield for isomerization of c-A vs t-A indicates that more rapid twisting about the double bond is not responsible for the shorter singlet lifetime of the cis isomer.



(1)

Since the focus of this investigation was the singlet-state reactions of the anetholes, their triplet-sensitized reactions received only cursory attention. In agreement with the nonquantitative observations of Nozaki et al.,[12] we observed that triplet sensitization using Michler's ketone and 365-nm irradiation results in more efficient photoisomerization than direct irradiation and that prolonged triplet-sensitized irradiation fails to produce even trace amounts of dimers. The photostationary state obtained with Michler's ketone is 68 ± 2% c-A. Quantum yields for triplet-sensitized isomerization were determined for acetonitrile solutions containing Michler's ketone (3 × 10^{-3} M) and t-A or c-A (0.05 M). The measured quantum yields for triplet-sensitized isomerization (Table II) are substantially larger than those obtained upon direct irradiation. Since it has not been established that energy transfer is completely efficient under our reaction conditions, the measured values represent lower bounds for the actual triplet isomerization quantum yields. Larger quantum yields, but a similar photostationary state, were reported by Caldwell et al.[13] for the benzophenone-sensitized photoisomerization of β-methylstyrene.

While intersystem crossing followed by triplet isomerization could account for the isomerization observed upon direct irradiation, more extensive sensitization and quenching experiments would be necessary to test this possibility. The role of intersystem crossing in phenylalkenes remains a topic of controversy in the photochemical literature.[6,9,10] Bonneau[9] reports a value of 3 × 10^7 s^{-1} for the rate constant of intersystem crossing for several phenylalkenes. A similar value (5 × 10^7 s^{-1}) would be necessary in order for intersystem crossing to be the major nonradiative decay pathway for t-A.

Table IV. Quantum Yields for Photodimerization of the Anetholes[a]

concn, M	Φ_1 (trans)	Φ_2 (cis)	Φ_3 (cis)
0.01	0.015		
0.02	0.037	0.0054	0.0040
0.03		0.0067	0.0046
0.04	0.064	0.010	0.0069
0.06	0.085	0.016	0.0088
0.08	0.099	0.021	0.010
0.10		0.027	0.013

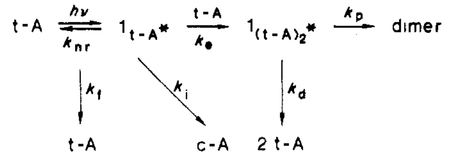
[a] Data for 313-nm irradiation of deoxygenated acetonitrile solutions.

Table V. Quantum Yields and Kinetics for Photodimerization of the Anetholes[a]

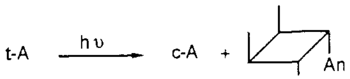
isomer	Φ_d[b]	$k_e\tau$, M^{-1}	$10^{-8}k_e$, M^{-1} s^{-1}
trans	0.56 ± 0.05	2.9 ± 0.3	3.2 ± 0.3
cis	0.56 ± 0.1	0.49 ± 0.2	0.8 ± 0.4

[a] Data for 313-nm irradiation of deoxygenated acetonitrile solutions. [b] Limiting quantum yield at infinite concentration.

Scheme I



Photodimerization Products and Kinetics. As previously reported by Nozaki et al.,[12] irradiation of 0.25 M t-A in cyclohexane solution results in the formation of the syn head-to-head dimer **1** as well as c-A (eq 2). Even at conversions >50%, the recovered anethole is largely (ca. 70%) t-A and the only dimer detected is **1**. Similar results were obtained in cyclohexane and acetonitrile solution. Quantum yields for dimerization (Table IV) were determined for acetonitrile solutions of 0.01–0.10 M t-A with 313-nm irradiation. Conversions of t-A were <6% in all cases.



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(2)

A simplified mechanism for photoisomerization and dimerization to t-A via the lowest singlet state is outlined in Scheme I. As discussed in the preceding section, the isomerization process (k_i) may involve intersystem crossing. According to this mechanism, the concentration dependence of the isomerization and dimerization quantum yields are given by eq 3 and 4. A plot

$$\frac{\Phi_i^0}{\Phi_i} = 1 + k_e\tau[\text{t-A}] \tag{3}$$

$$\frac{1}{\Phi_d} = \frac{k_p + k_d}{k_p}\left(1 + \frac{1}{k_e\tau[\text{t-A}]}\right) \tag{4}$$

of Φ_i^0/Φ_i vs [t-A] has an intercept of 1.01 and a slope ($k_e\tau$) of 2.5 M^{-1} (r = 0.97) and a plot of Φ_d^{-1} vs $[\text{t-A}]^{-1}$ has an intercept of 1.8 and a slope of 0.63 (r = 0.98), providing a limiting value of Φ_d = 0.56 and $k_e\tau$ = 2.9 M^{-1}. The reasonable agreement in $k_e\tau$ values from the isomerization and dimerization data provides support for the singlet dimerization mechanism outlined in Scheme I. From the measured singlet lifetime (Table I) and $k_e\tau$ values, a value of k_e = (3.2 ± 0.3) × 10^8, M^{-1} s^{-1} is calculated. Quantum yield and kinetic data for dimerization are given in Table V.

Irradiation of c-A in benzene or acetonitrile solution results in the formation of t-A and dimers **2** and **3** (eq 5). Results obtained for 313-nm irradiation of 0.05 M anethole (99.5% cis, 0.5% trans) during a 10-h irradiation period (11% consumption of c-A) are shown in Figure 1. Isomerization is seen to be more efficient than dimerization during the initial stages of the reaction

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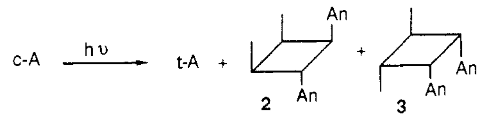
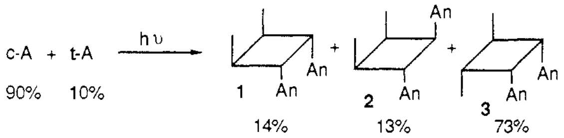


(5)

and causes the ratio of dimers **2**/**3** to decrease as the reaction progresses. Quantum yields for formation of dimers **2** and **3** (Table IV) were measured for acetonitrile solutions of 0.02–0.10 M c-A irradiated for 2 h (3% conversion). The ratio of dimers **2**/**3** increases with increasing concentration.

The results obtained with c-A are suggestive of the formation of **2** via the reaction of singlet c-A and of **3** via the reaction of singlet t-A with ground-state c-A. The stronger 313-nm absorbance, longer singlet lifetime (Table II), and higher dimerization efficiency (Table V) of t-A vs c-A all indicate that even the very small amount (0.5%) of trans isomer present may compete effectively with the cis isomer in the formation of dimers under our reaction conditions. In order to test this possibility, a 0.05 M acetonitrile solution consisting of 90% c-A and 10% t-A was irradiated at 313 nm, at which wavelength approximately half of the light is absorbed by each isomer. After 2 h of irradiation (<5% conversion) the isomer ratio has not changed and a mixture of dimers **1**–**3** is obtained (eq 6). The major product, dimer **3**, and dimer **1** are presumably formed from the reaction of singlet t-A with ground-state c-A and t-A, respectively. The ratio of dimers **3**/**1** = 5.2 is smaller than the 9/1 concentration ratio, indicative of less frequent reaction of singlet t-A with the c-A vs t-A ground state. Minor dimer **2** is presumably formed from the reaction of singlet c-A with ground-state c-A. The ratio of dimers **2**/(**3** + **1**) = 0.15 is similar to the ratio $\Phi_2/\Phi_1 = 0.16$ obtained from irradiation of the pure isomers (data from Table IV for 0.04 M solutions).



(6)

The results obtained for irradiation of anethole solutions containing 99.5% and 90% cis isomer appear to be uniquely consistent with the formation of **2** via photodimerization of c-A and of **3** via reaction of singlet t-A with ground-state c-A. Analysis of the quantum yield data for formation of dimer **2** (Table IV) using eq 4 provides an intercept = 1.8 and slope = 3.7 (r = 0.99) from which the limiting quantum yield $\Phi_2 = 0.51$ and $k_e\tau = 0.49$ M^{-1} can be calculated. From the measured singlet lifetime (Table I) and $k_e\tau$ values, a value of $k_e = 8.0 \times 10^7$ M^{-1} s^{-1} is calculated for the reaction of singlet and ground-state c-A (Table V). With use of the value of $k_e\tau$ and eq 3, the extent of self-quenching of singlet c-A by 0.1 M c-A is ca. 5%, in accord with the absence of detectable self-quenching of Φ_i by c-A (Table III).

Photodimerization Stereochemistry and Mechanism. The structure of dimer **1** was established by Nozaki et al.[12] by ^{1}H NMR analysis and by chemical conversion to the known (1α,2α,3β,4β)-1,2-dimethyl-3,4-diphenylcyclobutane. The symmetric head-to-tail structure of **1** is consistent with its ^{13}C NMR spectrum and mass spectral decomposition to dimethoxystilbene and t-A fragments (see the Experimental Section). We have prepared the all-trans dimer **4**, the major product of cation radical dimerization, by the method of Bauld and co-workers,[14] but we are unable to detect **4** as a product (<5%) of t-A photodimerization.

Preferential formation of syn-dimers has previously been observed for direct irradiation of styrene,[15] of its *p*-methoxy[16a] and *p*-dimethylamino[16b] derivatives, and of *trans*-stilbene.[17] Anti dimers predominate in triplet-sensitized[15] and electron transfer initiated styrene dimerizations.[16] The preference for syn dimer formation upon direct irradiation is attributed to the formation of a singlet excimer intermediate with maximum π-orbital overlap.[15-18] While styrene excimer fluorescence has not been observed, singlet excimer formation is consistent with the observed concentration dependence of singlet lifetimes, isomerization efficiency, and cyclodimerization efficiency, as well as the dimer stereochemistry.

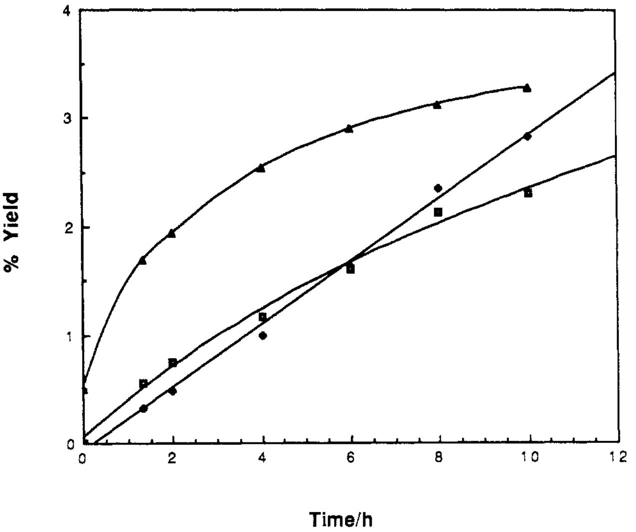
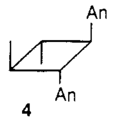


Figure 1. Concentrations of dimers **2** (□) and **3** (◆) and *trans*-anethole (▲) obtained upon irradiation of 99.5% *cis*-anethole to a conversion of 11.3%.

The absence of dimer formation upon triplet-sensitized irradiation of t-A or c-A deserves comment in view of the reported benzophenone-sensitized dimerization of styrene.[15] Both phenylalkenes and anisylalkenes are reported to have moderately long-lived triplets (30 ns for t-A) with twisted 1,2-biradical structures.[19] Thus the absence of triplet dimerization from t-A or c-A is not a consequence of a short triplet lifetime. It seems likely that the twisted triplet is unable to form a sandwich-type exciplex and thus can add to ground-state olefins only by a radical-type mechanism. A radical addition mechanism could account for the observation of triplet dimerization for the terminal-alkene styrene, but not for internal olefins such as t-A or c-A.

The assignment of head-to-head structure for dimers **2** and **3** formed upon irradiation of c-A is supported by their mass spectral fragmentation. The formation of dimer **2** in the cation radical dimerization of *cis*-anethole has been described by Bauld and co-workers but spectral data has not been reported.[14] A nonsymmetrical structure is indicated by the ^{13}C NMR and the aliphatic region of the spectrum is virtually identical with that of the [2 + 2] adduct of singlet *trans*-stilbene and *cis*-2-butene.[3] Dimer **3** also has a nonsymmetrical ^{13}C NMR spectrum and hence its stereochemistry can be assigned by a process of elimination. The other two possible head-to-head dimers of c-A are **5** and **6**, both of which should display symmetrical NMR spectra. We have synthesized **5** independently and confirmed that it is not a product of direct irradiation.[19]



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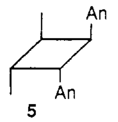

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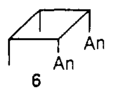

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The formation of dimer **3** as the predominant product of the reaction of singlet t-A with ground-state c-A is consistent with

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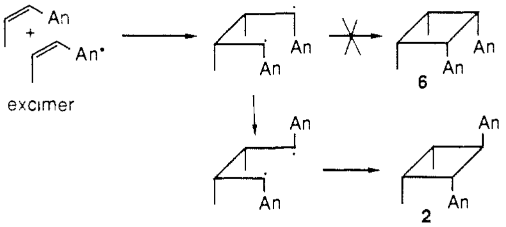
Scheme II



the formation of a heteroexcimer intermediate with maximum π-orbital overlap. The retention of c-A stereochemistry has previously been observed in its [2 + 2] cycloaddition reactions with singlet acetaldehyde[21a] and with singlet 9-cyanophenanthrene,[5] the latter reaction yielding the syn adduct. Analogous results have been obtained in a large number of [2 + 2] cycloaddition reactions of singlet-state molecules with ground-state cis olefins.[2-5] c-A is less reactive than t-A in its photocycloaddition reactions with 9-cyanophenanthrene[5] and 6-methylphenanthridine.[21b] From the results obtained in the anethole cross-dimerization (eq 6), we estimate that singlet t-A reacts with ground state c-A at approximately half the rate of reaction with t-A.

Unlike the stereospecific reaction of singlet t-A with ground-state t-A or c-A to give the syn dimers **1** and **3**, the dimerization of c-A gives predominantly the anti dimer **2**, with inversion of configuration, in one of the two reactants. To our knowledge, this is the first example of both the singlet dimerization of a cis aryl olefin and of inversion of stereochemistry in a singlet [2 + 2] cycloaddition reaction.

Several mechanisms for the formation of dimer **2** upon reaction of singlet c-A and ground-state c-A via a singlet excimer might be considered. Among these are the following: (a) cis → trans isomerization within the excimer followed by concerted $[2_s + 2_s]$ cycloaddition, (b) partial twisting within the excimer followed by concerted $[2_s + 2_a]$ cycloaddition, (c) intersystem crossing within the excimer followed by stepwise triplet cycloaddition, and (d) stepwise cycloaddition of the singlet excimer. Mechanisms (a) and (b) require twisting about a C=C bond which would destroy the orbital overlap necessary for excimer association. There is, to our knowledge, no example of isomerization of an aryl olefin singlet excimer; however, aryl olefin singlet exciplexes are known to yield locally excited aryl olefin triplets upon intersystem crossing.[22] Mechanism (c) would require that cycloaddition occur via a triplet excimer, a species generally found to dissociate into monomer triplet and monomer ground state.[23] Triplet aryl olefins, including the anetholes and stilbenes, fail to undergo triplet-state cyclodimerization.[22b] In mechanisms (c) or (d) formation of a single covalent bond would yield a triplet or singlet 1,4-biradical which might well be reluctant to form an all-cis 1,2,3,4-tetrasubstituted cyclobutane. Instead the biradical may undergo a one-bond rotation prior to formation of **2**. The singlet biradical from mechanism (d) might undergo intersytem crossing prior to bond rotation. A generalized biradical mechanism which does not specify spin multiplicity is outlined in Scheme II.

While the singlet-state concerted $[2_s + 2_s]$ cycloaddition in a symmetry-allowed process,[1] more detailed analysis of the potential energy surfaces for [2 + 2] cycloaddition[24] indicates that bond formation may not be concerted. The potential energy surfaces derived by Michl and co-workers[24] from their analysis of the H_2 + H_2 reaction is shown in Figure 2. According to the model, the excimer or exciplex formed upon association of the singlet and ground-state olefins must overcome a small thermal barrier in order to reach a second intermediate, the pericyclic minimum, which results from an avoided crossing of the reactant and product ground state surfaces. Caldwell and Creed[25] attempted to demonstrate that the pericyclic minimum might be a common intermediate in cycloaddition and cycloreversion processes, but they concluded that there was no experimental evidence for a singlet pericyclic minimum of finite lifetime corresponding to the well-known 1,4-biradical intermediates in triplet-state cycloaddition reactions. While we favor a singlet biradical mechanism for the formation of **2** (Scheme II), the behavior of the cis,cis case is clearly exceptional, and thus the biradical mechanism may not apply to "normal" singlet [2 + 2] cycloaddition reactions.

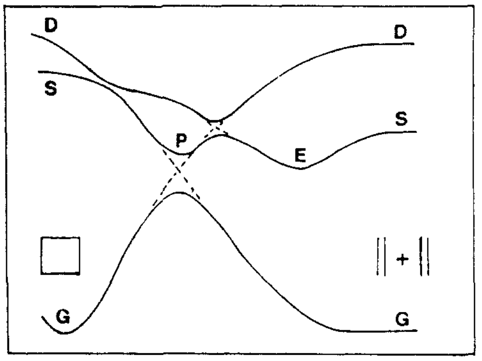


Figure 2. Schematic of the potential energy surfaces for [2 + 2] cycloaddition in the ground (G), singlet (S), and doubly excited (D) states. E is the exciplex and P is the pericyclic minimum.

Experimental Section

General Methods. ^{13}C NMR spectra were recorded on a JEOL FX-270 spectrometer with TMS as an internal standard. Ultraviolet and visible absorption spectra were measured with a Hewlett-Packard 8452A diode-array spectrophotometer. Mass spectra were determined with a Hewlett-Packard 5985 GC/MS system using an ionizing voltage of 70 eV. Fluorescence spectra were recorded on a Perkin-Elmer MPF-44A spectrophotometer. Fluorescence quantum yields were determined relative to styrene ($\Phi_f = 0.24$)[8] for solutions of matched absorbance (0.1) at the excitation wavelength (266 nm). Fluorescence lifetimes were measured on a PRA photon-counting apparatus. The light source of 313-nm irradiation was a 450-W Hanovia medium-pressure mercury lamp enclosed in a water-cooled Pyrex glass well. A potassium chromate solution filter was used to isolate the 313-nm line, and Corning glass filters 7-54 and 0-52 were used to isolate the 365-nm line. Analytical-style irradiations and quantum-yield measurements were conducted under dry N_2 in 13-mm-o.d. Pyrex tubes on a merry-go-round apparatus in a temperature-controlled water bath. Triplet-sensitized reactions were conducted on vacuum line degassed samples sealed in Pyrex tubes.

Irradiated mixtures were analyzed on a Hewlett Packard 5890A gas chromatograph equipped with a 10 m × 0.53 mm glass column packed with polydimethylsiloxane for analysis of the c-A, t-A, and dimers. This chromatograph is equipped with flame-ionization detectors. Light intensities were determined with *trans*-stilbene[17] (313 mm) or Aberchrome 540[26] (313 or 365 nm) actinometers.

Materials. Solvents were all spectra grade. Actonitrile (Aldrich) was distilled from calcium hydride prior to use. Hexane (Malinckrodt) and benzene (Aldrich) were distilled prior to use. *trans*-Anethole (Aldrich) was distilled prior to use and contained <0.7% *cis*-anethole by GC analysis. Cis-Anethole was prepared via Micheler's ketone sensitized isomerization of *trans*-anethole by using the method of Futamura et al.[21] Spinning band distillation yielded *cis*-anethole containing 0.5% *trans*-anethole.

(1α,2α,3β,4β)-1,2-Bis(4-methoxyphenyl)-3,4-dimethylcyclobutane (1). Dimer **1** was prepared by using a modification of the literature method.[12] A solution of *trans*-anethole (3.75 g, 25 mmol) in cyclohexane (100 ml) was irradiated with a Hanovia 450-W high-pressure mercury lamp through a Pyrex filter under nitrogen atmosphere for 24 h. After evaporation of the reaction mixture, anetholes (0.9 g, cis/trans = 30/70) were recovered and dimer **1** (1.3 g, 35%) was isolated by flash column chromatography (silica gel, benzene). The purity of **3** was 95% by GC analysis. **1**: ^{13}C NMR ($CDCl_3$) δ 157.4 (s), 13.5 (s), 129.1 (d), 113.2

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(d), 55.1 (q), 49.4 (d), 34.5 (d), 15.2 (q); mass spectrum, *m/e* 240 (0.5), 148 ($M^+/2$, 100).

(1α,2β,3α,4α)-1,2-Bis(4-methoxyphenyl)-3,4-dimethylcyclobutane (2). Dimer **2** was prepared by the method of Bauld and co-workers.[3] To a solution containing tris(4-bromophenyl)aminium hexachloroantimonate ($(4\text{-}BrC_6H_4)_3NSbCl_6$, 1 g, 1.22 mmol) in dichloromethane (100 ml), anethole (cis/trans = 90/10, 5.1 g, 34.5 mmol) was added at 0 °C under nitrogen. After 15 min the reaction was quenched by MeONa/MeOH (250 ml). GC analysis showed the reaction mixture was predominantly a ca. 1:1 mixture of dimers **2** and **4**. The dimers could not be separated from one another by preparative GC or column chromatography; however, the NMR spectrum of **2** could be assigned by subtraction of the signals from an authentic sample of dimer **4**.[13] ^{13}C NMR data for dimer **4** and the diphenyl analogue of **2** are reported below. **2**: ^{13}C NMR ($CDCl_3$) δ 157.8 (s), 136.0 (s), 129.0 (d), 128.7 (d), 113.7 (d), 113.5 (d), 55.0 (q), 48.0 (d), 27.5 (d), 34.5 (d), 14.3 (q), 10.8 (q); mass spectrum, *m/e* 240 (2.6), 148 ($M^+/2$, 100).

(1α,2β,3α,4β)-1,2-Bis(4-methoxyphenyl)-3,4-dimethylcyclobutane (4):[13] ^{13}C NMR ($CDCl_3$) δ 158.0 (s), 135.8 (s), 127.7 (d), 113.7 (d), 55.0 (q), 52.6 (d), 43.3 (d), 18.9 (q).

(1α,2β,3α,4α)-1,2-Dimethyl-3,4-diphenylcyclobutane:[3] ^{13}C NMR ($CDCl_3$) δ 48.4 (d), 46.4 (d), 37.6 (d), 34.6 (d), 14.4 (q), 10.8 (q).

(1α,2α,3α,4β)-1,2-Bis(4-methoxyphenyl)-3,4-dimethylcyclobutane (3). Dimer **3** was obtained from the direct irradiation of 1 g of anethole (6.7 mmol, cis/trans = 85/15) in acetonitrile (100 ml) with a Hanovia 450-W high-pressure mercury lamp for 24 h under nitrogen atmosphere. Flash chromatography (silica gel/benzene) yielded a mixture of dimers **3**, **2**, and **1** in a ratio of 70:17:13 as established by GC analysis. The presence of dimers **1** and **2** did not interfere with the NMR assignment of dimer **3**: ^{13}C NMR ($CDCl_3$) δ 157.3 (s), 157.2 (s), 133.8 (s), 131.3 (d), 127.8 (d), 113.4 (d), 112.8 (d), 54.8 (q), 54.7 (q), 47.5 (d), 47.1 (d), 41.8 (d), 39.5 (d), 20.4 (q), 14.6 (q); mass spectrum, *m/e* 240 (2.6), 148 ($M^+/2$, 100).

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Registry No. 1, 19043-23-3; **2**, 84107-48-2; **3**, 117467-12-6; **4**, 84107-47-1; t-A, 4180-23-8; c-A, 25679-28-1.

Electron Transfer Induced Photoisomerization, Dimerization, and Oxygenation of *trans*- and *cis*-Anethole. The Role of Monomer and Dimer Cation Radicals

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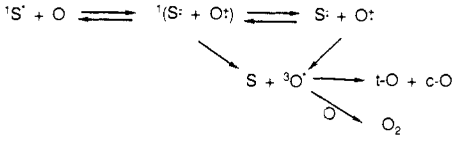
Abstract: Irradiation of *trans*- or *cis*-anethole in the presence of electron acceptors results in cis,trans isomerization, cyclodimerization, and (in the presence of oxygen) oxidative cleavage. The initial step in each of these reactions is photoinduced electron transfer to yield a singlet radical ion pair. Anethole cation radicals are the initial reactive intermediates formed in each reaction. Isomerization occurs via reverse electron transfer to generate triplet anethole which decays to a mixture of cis and trans isomers. Dimerization occurs via the [2 + 1] cycloaddition of a cation radical and a neutral which proceeds with retention of olefin configuration to yield a mixture of syn and anti head-to-head dimers. The syn/anti dimer ratio is sensitive to reaction conditions because of the lower stability of the syn vs anti dimer cation radical. Reaction of the monomer cation radical with O_2^- or O_2 results in formation of *p*-anisaldehyde. It is unlikely that an acyclic 1,4-cation radical is the precursor of any of the observed products.

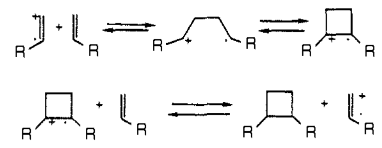
The cation radicals of electron-rich olefins can be readily generated by photoinduced electron transfer to a suitable acceptor.[1] Among the most extensively investigated reactions which occur via olefin cation radical intermediates are the cis,trans isomerization of internal olefins and the dimerization of terminal olefins.[1a] Both isomerization[2] and dimerization[3] can occur via triplet mechanisms in which photoinduced electron transfer from the olefin (O) to a singlet acceptor ($^*S^1$) generates a singlet radical ion pair which can undergo reverse electron transfer to yield the locally excited olefin triplet (Scheme I). The resulting isomerization and dimerization processes are analogous to those obtained via conventional triplet sensitization.

Of greater current mechanistic interest are isomerization and dimerization processes with quantum yields greater than 1.0 in which the cation radical is the reactive intermediate in a chain process. The mechanism outlined in Scheme II was originally proposed by Ledwith[4] to account for the triplet chloranil sensitized reaction of *N*-vinylcarbazole to yield the head-to-head trans dimer and has subsequently been invoked to account for the [2 + 2] cyclodimerization of numerous enamines,[4] vinyl ethers,[5] styrenes,[6] and acetylenes.[7] We recently proposed a cation radical chain mechanism for the one-way isomerization of *cis*-stilbene.[8] The proposed mechanism requires unimolecular cis → trans cation radical isomerization, a process which we have subsequently found

Scheme I



Scheme II



[†] Visiting scholar on leave from Shinshu University, Matsumoto, Japan.

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